

UNIVERSITÉ DE MONTRÉAL

REGIONALIZED AQUATIC ECOTOXICITY CHARACTERIZATION FACTOR FOR ZINC
SOIL EMISSIONS ACCOUNTING FOR SPECIATION AND FOR THE TRANSFER
THROUGH GROUNDWATER

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DEDICATION

To my beloved husband and my two Incredibles: Istvan and Ariadne

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RÉSUMÉ

L'analyse du cycle de vie (ACV) est une évaluation des impacts environnementaux d'un produit, d'un processus ou d'un service tout au long de son cycle de vie. Cette évaluation est faite pour une fonction spécifique d'un produit ou d'un processus (par exemple: la fonction de séchage des mains pour un sèche-mains ou de fournir un service de nettoyage pour une entreprise de nettoyage). Le cycle de vie d'un produit peut inclure l'extraction de matières premières, l'acquisition d'énergie, sa production et sa fabrication, son utilisation, sa réutilisation, son recyclage et son élimination finale (fin de vie). Toutes ces étapes du cycle de vie d'un produit contribuent à la production des déchets, des émissions et les consommations des ressources. Ces échanges environnementaux contribuent aux impacts tels que le changement climatique, l'appauvrissement de l'ozone stratosphérique, la formation de photooxydants (smog), l'eutrophisation, l'acidification, le stress toxicologique sur la santé humaine et les écosystèmes, l'épuisement des ressources et la pollution sonore. L'ACV permet de voir où un produit ou un service peut être amélioré ou de fabriquer de meilleurs produits. L'évaluation des impacts environnementaux de cycle de vie est la troisième phase d'ACV dans laquelle le flux de matériaux associés au produit (ou processus) est traduit en consommations de ressources et impacts potentiels sur l'environnement. L'objectif de la phase d'analyse d'impact est donc d'interpréter les inventaires des émissions du cycle de vie et de la consommation des ressources en termes d'indicateurs et d'évaluer l'impact sur les entités que l'on veut protéger.

USEtox est un modèle consensuel d'évaluation de l'impact du cycle de vie (ACVI) développé dans le cadre de l'Initiative du cycle de vie du PNUE-SETAC (UN environment programme- Society for environmental toxicology & chemistry). Le développement de ce modèle était une tentative de réduire la variabilité des différents résultats obtenus en utilisant différents modèles d'ACV. Le modèle nous permet de calculer les FC (c'est-à-dire la quantité d'impact environnemental par quantité de substance émise, facteur de caractérisation) pour la toxicité humaine et l'écotoxicité, qui est un produit du facteur d'effet (FE) et du facteur du devenir (FF). L'écotoxicité des métaux est considérée comme mal modélisée par USEtox car la spéciation des métaux n'est pas incluse dans le cadre de calcul.

Lors du consensus de Clearwater, la nécessité de tenir compte de la spéciation des métaux a été identifiée comme l'une des principales priorités par un groupe d'experts pour améliorer l'évaluation de l'impact écotoxicologique des métaux dans l'ACV. Le facteur de biodisponibilité (BF) est inclus

dans la définition de CF ($CF = EF \cdot BF \cdot FF$) qui est le rapport de la concentration de métal ‘true’ solution (ions libres et paires d’ions) sur la concentration ‘total’ de métal. Pour être cohérent avec l’inclusion du facteur de biodisponibilité dans les FC, il a également été recommandé d’inclure la spéciation lors du calcul du facteur d’effet (FE). Actuellement, les chercheurs utilisent le ‘Free Ion Activity Model (FIAM)’ (FIAM) et le ‘Biotic Ligand Model’ (BLM) pour prédire l’effet de la concentration de métal dans le milieu aquatique, compte tenu de la spéciation. Le BLM utilise une approche mécaniste basée sur l’hypothèse que l’interaction métal-ligand biotique peut être représentée comme n’importe quelle autre réaction chimique d’une espèce métallique avec un ligand organique ou inorganique.

Dans la version actuelle de USEtox, le compartiment ‘Soil’ est considéré comme un ‘*sink*’ pour les substances: le sort de la fraction de contaminant qui atteint le compartiment des eaux souterraines par le sol ‘*disappears*’ et n’est jamais transféré dans les eaux de surface. Cela peut être une hypothèse appropriée pour la plupart des produits chimiques organiques, ce qui peuvent être dégradés avant la résurgence des eaux souterraines que l’écoulement des eaux souterraines est lent, mais cette hypothèse peut représenter un biais important pour les métaux, qui ne sont pas biodégradables et peuvent voyager du sol dans les eaux souterraines par les couches de sol plus profondes, et finalement à l’eau douce. Le destin du métal peut donc ne pas être correctement traité dans USEtox.

La plupart des aquifères et des nappes phréatiques sont interconnectés avec les masses d’eau douce et les mouvements d’eau entre les eaux souterraines et les eaux de surface constituent une voie majeure de transfert de substances chimiques entre les systèmes terrestres et aquatiques. En ne tenant pas compte du sort des métaux dans les eaux souterraines, le sort des métaux dans le sol est surestimé (qui apparaît comme le dernier compartiment où la majeure partie du métal rejeté dans le sol «disparaît») et le devenir du métal dans l’eau de surface est sous-estimée (car les métaux atteignant les eaux souterraines n’atteignent jamais potentiellement l’eau de surface dans le modèle).

Après les précipitations, une fraction de l’eau de pluie s’infiltre à travers la surface terrestre et se déplace verticalement vers le bas jusqu’à la nappe phréatique. L’eau souterraine se déplace alors lentement à la fois verticalement et latéralement avec un écoulement tri-dimensionnel qui se déplace le long des trajets d’écoulement de longueurs variables allant des zones de recharge aux

zones de décharge. Un bassin versant (analogue à un «bassin hydrographique» ou «bassin versant») est défini comme une zone de drainage des eaux de pluie jusqu'à ce qu'elle atteigne le même plan d'eau (une rivière, un lac ou l'océan). Les limites des bassins versants sont basées sur la topographie du sol et les cours d'eau. Le bassin versant peut être considéré comme le niveau de résolution géographique auquel toute goutte de pluie qui tombe sur le sol atteindra le même plan d'eau (et tous les contaminants transportés par ce courant d'eau).

L'estimation du comportement des eaux souterraines nécessite une modélisation de l'interaction entre tous les processus importants du cycle hydrologique, tels que la couverture terrestre, le profil du sol, l'infiltration, le ruissellement, l'évapotranspiration, la fonte des neiges et les variations des eaux souterraines. La description quantitative des processus hydrologiques peut devenir très compliquée en raison de l'incertitude et de la complexité élevées des paramètres physiques sous-jacents. Cependant, dans le ACVI, l'évaluation des impacts toxiques est généralement réalisée en utilisant des modèles d'état d'équilibre simplifiés tels que USEtox. L'un des principes importants de USEtox est d'être parcimonieux et d'inclure uniquement les mécanismes environnementaux les plus pertinents. Par conséquent, l'intégration du transfert des contaminants dans les eaux souterraines dans ACVI devrait également être effectuée avec parcimonie dans une version adaptée de USEtox, permettant seulement de quantifier la masse de contaminant transférée du sol à l'eau de surface à l'état stationnaire, sans détails sur la voie du contaminant dans le compartiment de sous-sol/ des eaux souterraines et sur la cinétique des processus hydrologiques. L'objectif de la présente étude est de développer une telle version de USEtox pour calculer les facteurs de caractérisation écotoxicologiques des eaux souterraines (CF) pour une émission dans les sols, en tenant compte de la spéciation dans tous les compartiments environnementaux (sol, sous-sol et eau souterraine, eau douce) et de l'appliquer au cas du zinc.

Pour le calcul du facteur de devenir (FF) et du facteur de caractérisation (FC) en considérant l'émission de Zn dans le sol, les calculs sont effectués en plusieurs étapes: d'abord, les coefficients de partage sol / eau du sol et du sous-sol sont calculés en utilisant le logiciel de spéciation WHAM7 pour toutes les différentes unités de sol et de sous-sol de la base de données mondiale harmonisée sur les sols (HWSD). Deuxièmement, des calculs de spéciation sont également effectués dans le compartiment d'eau douce, sur la base des données disponibles sur les propriétés de l'eau douce partout dans le monde et en utilisant le modèle de spéciation WHAM. Troisièmement, un système d'information géographique est utilisé pour recouper les unités de sol et les bassins versants afin

d'obtenir des cellules géographiques (cellules de résolution native). Dans chacune de ces cellules, on considère que Zn a les coefficients de partage sol-eau pour les compartiment des sol et sous-sol correspondant à sa spéciation dans ces compartiments et aussi que Zn a des coefficients de partage solide-eau suspendu et octanol-eau correspondant de sa spéciation dans l'eau pour ce bassin versant spécifique. Quatrièmement, USETox est modifié en reliant a) le sol au sous-sol et au compartiment des eaux souterraines et b) le sous-sol et le compartiment des eaux souterraines au compartiment d'eau douce. Les facteurs de devenir du sol à l'eau (FF_{sw}) pour chaque cellule de résolution naturelle sont calculés en utilisant ces coefficients de partage du sol, du sous-sol et du bassin versant dans la version modifiée d'USETox. Ces FF_{sw} spécifiques aux cellules de résolution native sont multipliées par des facteurs de biodisponibilité spécifiques (BF) et des facteurs d'effets (EF) pour générer des facteurs de caractérisation du sol (CF_{sw}) pour toutes les cellules de résolution native disponibles dans le monde entier. Cinquièmement, les résultats obtenus à l'échelle de la résolution native sont agrégés à différentes échelles de régionalisation plus opérationnelles: bassin versant, pays, continent et niveau global, avec la détermination de la variabilité spatiale correspondante. Enfin, les résultats sont comparés aux valeurs par défaut calculées par USETox.

Les facteurs de caractérisation régionaux de l'écotoxicité des eaux douces pour le zinc émis dans le sol ont une variabilité spatiale globale sur 3 ordres de grandeur et la valeur globale moyenne pondérée est dans le même ordre de grandeur que la valeur USETox par défaut (1,42 fois inférieure). La variabilité spatiale des facteurs de sort du Zn du sol à l'eau (FF_{sw}) et des facteurs de caractérisation du Zn (CF_{sw}) dans chaque bassin versant est quantifiée. Les résultats sont illustrés sur une carte du monde pour toutes les cellules de résolution native pour lesquelles des données sont disponibles. À l'exception de l'Europe, tous les FF_{sw} et CF_{sw} régionaux et continentaux ont varié de plus de 2 ordres de grandeur. Pour l'Europe, une variabilité spatiale de 3 ordres de grandeur est observée parce que (1) la variabilité spatiale de la spéciation régionale dans le sol est plus grande (2) des données régionalisées pour l'eau douce sont disponibles pour de nombreux sites à travers le continent ainsi que à une plus grande variabilité spatiale de la spéciation dans l'eau.

L'une des principales limites de l'étude est la faible disponibilité des données régionalisées sur l'eau douce nécessaires à l'exécution du modèle de spéciation. Avec les données actuelles disponibles, la variabilité spatiale des CFs pour Zn à l'échelle continentale est proche de l'incertitude des CFs de l'USEtox (deux ordres de grandeur), ce qui signifie que l'utilisation d'un CF continentale semble un compromis raisonnable entre une collecte de données trop intensive et une évaluation d'impact imprécise.

ABSTRACT

Life cycle assessment (LCA) is the assessment of environmental impacts of a product, process or service across its entire life cycle. This assessment is done based on a particular function of the product or process (for example: the function of drying hands for a hand dryer or providing cleaning service for a cleaning company). A product's life cycle can include the extraction of raw materials, energy acquisition, its production and manufacturing, use, reuse, recycling and ultimate disposal. All these stages in a product's life cycle result in the generation of wastes, emissions, and the consumption of resources. These environmental exchanges contribute to impacts such as, climate change, stratospheric ozone depletion, photooxidant formation (smog), eutrophication, acidification, toxicological stress on human health and ecosystems, depletion of resources, and noise pollution among others. LCA allows us to see where a product or service can be improved or manufacturing of new better products. Life cycle impact assessment is the third phase of LCA in which the flow of materials associated with the product (or process) is translated into consumptions of resources and potential impacts to the environment. The purpose of the impact assessment phase is thus to interpret the life cycle emissions and resource consumption inventory in terms of indicators and to evaluate the impact on the entities that we want to protect.

USEtox is a consensual life cycle impact assessment (LCIA) model developed within the UNEP-SETAC Life Cycle Initiative. The development of this model was an attempt to reduce the variability of different results obtained from using different LCA models. The model allows us to calculate CFs (ie the quantity of environmental impact per quantity of substance emitted) for human toxicity and ecotoxicity which is a product of Effect Factor (EF) and Fate factor (FF). Metal ecotoxicity is considered as poorly modeled by USEtox as the metal speciation is not included within the calculation framework.

During the Clearwater consensus, the need to account for metal speciation has been identified as one of the key priorities by a group of experts to improve the ecotoxicological impact assessment of metals in LCA. The bioavailability factor (BF) is included within the definition of CF ($CF = FF \cdot BF \cdot EF$) which is the ratio of the true solution (free ions and ion pairs) metal concentration over total metal concentration. To be consistent with the inclusion of bioavailability factor in the CF, it was also recommended to include speciation while calculation the Effect Factor (EF). Currently, researchers use Free Ion Activity Model (FIAM) and Biotic Ligand Model (BLM) to predict the

effect concentration of metal in aquatic environment accounting for the speciation. BLM uses a mechanistic approach that is based on the hypothesis that the metal–biotic ligand interaction can be represented like any other chemical reaction of a metal species with an organic/inorganic ligand.

In the current version of USEtox, the soil compartment is considered as a sink for the substances: the fate of the fraction of contaminant that reaches the groundwater compartment through soil, “disappears” and is never transferred to the surface water. This may be an appropriate assumption for most organic chemicals, which may degrade before the resurgence of groundwater as the groundwater flow is slow. However, this assumption may represent an important bias for the metals, which are not biodegradable and may travel from soil to groundwater through the deeper soil layers, and ultimately to freshwater. The metal fate may therefore not be properly addressed within USEtox.

Most of the aquifers and groundwater table are interconnected with the freshwater bodies and water movement between groundwater and surface water is a major pathway for chemical transfer between terrestrial and aquatic systems. By not considering the fate of metal through groundwater, the fate of metals to the soil is overestimated (which appears as the ultimate compartment where most of the metal emitted to soil “disappears” from the system when transferred to groundwater) and the fate of metal to the surface water is underestimated (as metals reaching the groundwater never potentially reaches surface water in the model).

After precipitations, a fraction of the rainwater infiltrates through the land surface and moves vertically downward to the water table. The ground water then moves slowly both vertically and laterally with a three-dimensional flow, which moves along flow paths of varying lengths from areas of recharge to areas of discharge. A watershed (analogous with ‘drainage basin’ or ‘catchment area’) is defined as an area of land that drains down the precipitation until it reaches the same water body (a river, a lake or the ocean). Watershed boundaries are based on soil topography, watercourse and stream locations. The watershed can be considered as the geographical resolution level at which any raindrop that falls on the soil will reach the same water body (and so do all the contaminants transported by this water flow).

Estimation of the groundwater behaviour requires modelling of the interaction between all of the important processes in the hydrologic cycle, such as land cover, soil profile, infiltration, surface runoff, evapotranspiration, snowmelt and variations in groundwater. The quantitative description

of the hydrologic processes may become very complicated due to the high uncertainty and complexity in the underlying physical parameters. However, in LCIA, toxic impact assessment is generally conducted using simplified steady-state models such as USEtox. One of the important principles of USEtox is to be parsimonious and to include only the most relevant environmental mechanisms. Hence, the integration of the transfer of contaminant through groundwater in LCIA should also be done parsimoniously in an adapted version of USEtox, only allowing to quantify the mass of contaminant transferred from soil to surface water at steady state through groundwater, without details about the pathway of the contaminant in the subsoil / groundwater compartment and about the hydrologic processes kinetics. The objective of the present study is to develop such a version of USEtox to calculate regionalized freshwater ecotoxicity characterization factors (CF) for metal soil emissions accounting for the missing link from topsoil to freshwater through groundwater and considering speciation in all the environmental compartments (soil, subsoil & groundwater, freshwater) and to apply it to the case of Zinc.

For the soil to water fate factor (FF) and characterization factor (CF) calculation considering Zn emission to soil, calculations are performed in several steps: first, the soil/water partitioning coefficients (K_d) for Zn in soil and in subsoil is determined using the WHAM7 speciation software for all the different soil and subsoil units from the harmonized world soil database (HWSD). Second, speciation calculations are also performed in the freshwater compartment, based on available data about freshwater properties all over the world and using the WHAM speciation model. Third, a geographic information system is used to intersect soil units and watersheds to obtain some geographical cells (native resolution cells). In each of those cells, it is considered that Zn has soil-water partition coefficients in the soil and subsoil compartments corresponding to its speciation in those compartments and that Zn also has suspended solid-water and octanol-water partition coefficients in the surface water compartment corresponding to Zn speciation in water within that specific watershed. Fourth, USETox is modified by linking a) the soil to the subsoil & groundwater compartment and b) the subsoil & groundwater compartment to the freshwater compartment. Fate factors from soil to water (FF_{sw}) for each native resolution cell are calculated using these soil, subsoil and watershed level partition coefficients in the modified version of USETox. These native resolution cell specific FF_{sw}s are multiplied with watershed specific bioavailability factors (BFs) and effect factors (EFs) to generate soil to water characterization factors (CF_{sw}) for all the native resolution cells for which data is available around the globe. Fifth,

the results obtained at the native resolution scale are aggregated at different more operational regionalization scales: watershed, country, continent and global level, with the corresponding spatial variability determination. Lastly, the results are compared to the default values calculated by USETox.

Regionalized freshwater ecotoxicity characterization factors for zinc emitted to soil have a global spatial variability over 3 orders of magnitude and the weighted average global value is in the same order of magnitude than the default USETox value (1.42 times lower). The spatial variability of the Zn fate factors from soil to water (FF_{sw}) and of the Zn characterization factors (CF_{sw}) within each watershed is quantified. The results are illustrated on a world map for all the native resolution cells for which data is available. With the exception of Europe, all the regional and continental FF_{sw} and CF_{sw} varied over 2 orders magnitude. For Europe, a spatial variability of 3 orders of magnitude is observed because (1) the spatial variability of regional speciation in soil is larger (2) spatial data for freshwater is available for many locations across the continent thereby leading to a higher spatial variability of the speciation in water.

One of the main limits of the study is the low availability of regionalized freshwater data needed to run the speciation model. With the current available data, the spatial variability of Zn CFs at continental scale is close to the uncertainty of USEtox CFs (two orders of magnitude), meaning that using a continental level CF seems a reasonable compromise between a too intensive data collection and a too imprecise impact assessment.

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LIST OF SYMBOLS AND ABBREVIATIONS

BF	Bioavailability Factor
BLM	Biotic Ligand Model
CF	Characterization Factor
DOC	Dissolved Oxygen Content
EF	Effect Factor
FF	Fate Factor
LCA	Life Cycle Analysis
LCIA	Life Cycle Impact Analysis
OM	Organic Matter Content
SETAC	Society For Environmental Toxicology And Chemistry
TBLM	Terrestrial Biotic Ligand Model
UNEP	United Nations Environmental Program
WHAM	Windermere Humic Aqueous Model
Zn	Zinc

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CHAPTER 1 INTRODUCTION

In life-cycle analysis (LCA), metals' ecotoxicological impacts are always on the higher side. It is partly because of the consideration of the total metal concentration within the calculations. And also, all these models (IMPACTWorld, IMPACT2002, USES-LCA, CalTOX, LUCAS etc.) were initially built for organics later they were developed for metals. One of the many assumptions for the organic material were they are biodegradable and do not undergo speciation which is not true for the metals since they are persistent in nature, keep accumulating every day and can have variable valance states, thereby voiding the use of those models for metal toxicity calculations (Christensen et al., 2007; Haye, Slaveykova, & Payet, 2007; Pizzol, Christensen, Schmidt, & Thomsen, 2011a).

Even if one like to choose from the abovementioned model for metal toxicity calculations, all of the models vary in their scope and modeling principles. The inter-model results variations and uncertainty due to the assumptions are very high. Choosing a single model for specific calculations and making modifications and then adapting for others will introduce erroneous results (Pizzol et al., 2011a; Pizzol, Christensen, Schmidt, & Thomsen, 2011b).

USEtox model is developed as the results of scientific consensus among these model developers: CalTOX, IMPACT 2002, USES-LCA, BETR, EDIP, WATSON and EcoSense. The development of this model was an attempt to reduce the variability of different results from different LCA models. Through this process, the inter model variation was reduced from an initial range of up to 13 orders of magnitude down to no more than two orders of magnitude for any substance (Rosenbaum et al., 2008).

Moreover, integrating metal along with speciation and regionalization within LCA is challenging, given the lack of precise information on LCA emissions, choice of methods speciation calculations and inadequate model assumptions. The study on Zn by Ligthart, Jongbloed, and Tamis (2010) for gutter and downpipes using CML method showed a considerable decrease in the freshwater (25%) and marine aquatic ecotoxicity potential (42%) pointing to the fact that total metal concentration is in fact not a good indicator of metal fate. It also implies that total metal concentration is not responsible for detrimental effects on human health and ecosystems. It was recommended in the Clearwater workshop by Diamond et al. (2010) to include the bioavailability fractor of metal (the ratio of truly solution metal by total metal) which is considered to be the best indicator for toxic

effects in all fate and effect calculations. It was suggested the use of a geochemical speciation model, in particular the WHAM 6.0 model (Windermere Humic Aqueous Model, then available version) to obtain the bioavailable fraction and the use of archetypes of the same properties to consider the spatial variability of environmental properties (Diamond et al., 2010). Considerable progress have been made after the work done by Gandhi et al. (2010), Gandhi, Huijbregts, et al. (2011) and Gandhi, Diamond, et al. (2011) with Cu, Ni and Zn in case of aquatic ecotoxicity in terrestrial ecosystems in European freshwater. Dong, Gandhi, and Hauschild (2014) had implemented the previous method and extended the toxicity calculations on 14 cationic metals (Al, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Mn, Ni, Pb, Sr, Zn). (Diamond et al., 2010; Dong et al., 2014; Gandhi, Diamond, et al., 2011; Gandhi et al., 2010; Gandhi, Huijbregts, et al., 2011). Although WHAM 6 was tested for water, it was first evaluated and validated for soils first by Plouffe, Bulle, and Deschênes (2015). The calculated Zn characterization factors after incorporating the true solution Zn and soluble Zn by Plouffe, Bulle, and Deschênes (2016) are lower than the values calculated using traditional methods. The results point out the importance of considering speciation in heterogenous media like soils. However, it also raises the question that the soluble metal fractions might leach to the deeper soil layers and soil has a finite infiltration capacity.

In reality, the transfer of contaminants in the soil depends on physicochemical properties of the soil and the substance. The infiltration capacity of a soil determines whether and how much of the water can seep into the deeper soil layer. Groundwater represents one portion of the earth's water circulatory system known as the hydrologic cycle. It constitutes 0.39% of the world's water but 49% of the world's freshwater. Water-bearing formations of the earth's crust act as conduits for transmission and as reservoirs for storage of water. Water enters in these formations from natural recharges such as, precipitation, streamflow, lakes and reservoirs and travels slowly for varying distances until it returns to the surface by action of natural flow, plants or humans (Aral & Taylor, 2011; Bowen, 1979; "Groundwater Hydrology," ; Todd & Mays, 2005).

The objective of this study is to make modifications within USEtox considering the missing link from topsoil to freshwater through groundwater and considering speciation in all the environmental compartments (soil, subsoil & groundwater, freshwater) thereby calculating regionalized soil to freshwater Zn characterization factors (CF). The methodology proposed in this project is as follows. The use to WHAM 7 (latest version) to perform speciation with the regionalized soil properties available over the world from HWSD database (HWSD-database, 2014). After that, the

soluble Zn fraction from soil will be added with the modified version of the USETox model in which soil, groundwater and surface water system are connected. Soil to water fate and characterization factors will be calculated in native soil resolution. Calculations will also be performed for watershed specific resolution and aggregated fate and characterization factors over continents and regions. The results will be further compared with the USETox default results.

The first chapter of this thesis contains literature review followed by research hypothesis, justification of choice, objectives and methodology in Chapter 2. Chapter 3 is the manuscript from the project that has been submitted to the International Journal of LCA. Finally, Chapter 3 discusses the conclusion drawn and overall perspectives from the project.

CHAPTER 2 LITERATURE REVIEW

This chapter begins with the explanation of Life Cycle Analysis (LCA) and the various steps involved to perform a complete LCA. The challenges with metals in LCA in aquatic and terrestrial ecotoxicology are described and the choice of metal to be studied is justified. State of the art of the current mathematical modelling in LCA and the limitations are discussed toward the end.

2.1 Life Cycle Analysis (LCA)

2.1.1 Definition, Characteristics and Steps of LCA

Life cycle assessment is the assessment of environmental impacts of a product, process or service across its entire life cycle. This assessment is done based on a particular function of the product or process (for example: the function of drying hands for a hand dryer or providing cleaning service for a cleaning company). A product's life cycle can include the extraction of raw materials, energy acquisition, its production and manufacturing, use, reuse, recycling and ultimate disposal. All these stages in a product's life cycle result in the generation of wastes, emissions, and the consumption of resources. These environmental exchanges contribute to impacts such as, climate change, stratospheric ozone depletion, photooxidant formation (smog), eutrophication, acidification, toxicological stress on human health and ecosystems, depletion of resources, and noise pollution among others. LCA allows us to see where a product or service can be improved or manufacturing of new better products. According to the series of ISO14040 standards and SETAC (Society for Environmental Toxicology And Chemistry) definition, any LCA study should consist of four steps. The study begins with (1) Goal and scope definition, then (2) Life cycle inventory (LCI), (3) Life cycle impact assessment (LCIA) and finally (4) Interpretation (Michael Zwicky Hauschild et al., 2002; Jolliet, Saadé, Crettaz, & Shaked, 2010; Tillman & Baumann, 2004).

The first step deals with the definition and setting the objectives, a description and scope of the study, the type of application of LCA study (to be) performed, target audience, the stakeholders and the functional unit. The frontiers of the system and the reference flows are also defined in this step. Unlike other phases of the LCA, the phase is not very technical, but has a strong participatory dimension (Jolliet et al., 2010).

The next phase of LCA is to establish an inventory of all incoming and outgoing flows of the system during the stages of the life cycle. If all steps are considered, LCA will be called "cradle to grave" as opposed to LCA "cradle to gate" [at the factory]. In the latter type, the phases of use and end of life are excluded. It is useful for the assessment of the intermediate products which are not intended for the consumer. Inventory data can come from the same manufacturers and suppliers (primary data) or specialized databases (secondary data) such as ecoinvent (Canals et al., 2011; Jolliet et al., 2010).

The impact assessment step assesses the impact on the environment and emissions from extractions which were inventoried in the previous phase. This step sometimes can be broken down into four stages. This study will deal with metal contamination in aquatic and terrestrial ecosystem which fall within this very step and is discussed in more detail in section 2.2 (Jolliet et al., 2010).

Interpretation step allows to interpret the results in each of the preceding phases and also to assess uncertainties related with them. The key points and options for improvement of the product studied are well identified. This last phase can (also) be completed by linking it with the environmental aspects and economic or social aspects (Jolliet et al., 2010).

The four phases of LCA are presented in Figure 2-1 (Jolliet et al., 2010).

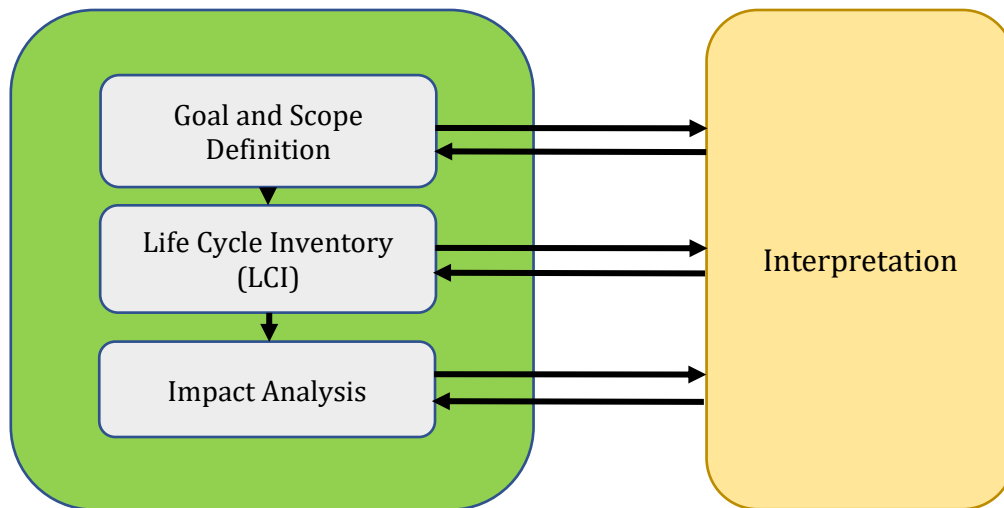


Figure 2-1 Framework (four phases) of LCA study

2.2 Life cycle impact assessment (LCIA)

In this third phase of LCA the flow of materials associated with the product (or process) is translated into consumptions of resources and potential impacts to the environment. The purpose of the impact assessment phase is thus to interpret the life cycle emissions and resource consumption inventory in terms of indicators for the Areas of Protection (AoPs), i.e. to evaluate the impact on the entities that we want to protect. The Areas of Protection (presented in Figure 2-2) considered according to ILCD (international Reference on Life Cycle Data System) handbook are: ‘Human Health’, ‘Natural Environment’ and ‘Natural Resources’ (Michael Hauschild et al., 2009a, 2009b).

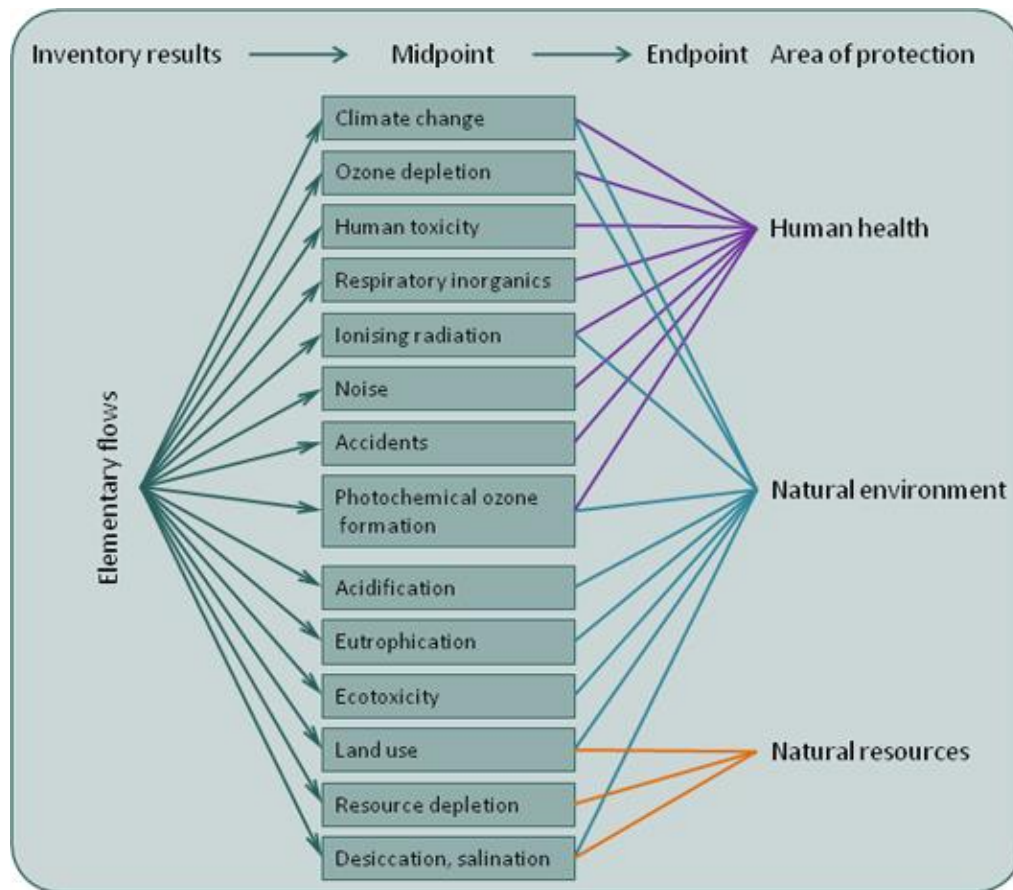


Figure 2-2 Impact categories for characterisation modelling at midpoint and endpoint (Areas of Protection) levels (Michael Hauschild et al., 2009b)

According to ISO 14044, Life Cycle Impact Assessment (LCIA) proceeds through four steps : *(a) Classification (mandatory)*: In this step, the elementary flows from the life cycle inventory are then assigned to impact categories according to the pollutant's ability to contribute to different environmental problems. *(b) Characterisation (mandatory)*: The relative contributions of the emissions and resource consumptions to each type of environmental impact are calculated in this step. *(c) Normalisation (optional)*: The characterised impact scores are associated with a common reference, such as the impacts caused by one person during one year in a stated geographic context. *(d) Weighting (optional)*: The different environmental impact categories and/or Areas of Protection are ranked according to their relative importance. Weighting is necessary when trade-off situations occur in LCAs, or comparing alternative products (Michael Hauschild et al., 2009b; Tillman & Baumann, 2004).

The path that is followed by any pollutant from its emission to final impact is called impact pathway. In LCIA, impacts on the Areas of Protection are modelled by applying knowledge about the relevant impact pathways or environmental mechanisms (Michael Hauschild et al., 2009a; Joliet et al., 2010).

Identification and quantification of impacts on human health and ecosystems due to emissions of toxic substances are very important for the development of sustainable products and technologies. Toxicity indicators (characterization factors) for human health effects and ecosystem quality are necessary both for comparative risk assessment and for LCAs applied to chemicals and emission scenarios. However, in practice, there are discrepancies and differences in results from using different models and they often fail to arrive at the same toxicity characterisation score for a substance (Rosenbaum et al., 2008).

Different LCIA methodologies and models have been developed over time: researchers have often updated and renovated their previously developed models and then released new versions (example: EDIP 97 was substituted by the more developed EDIP 2003). In some cases different research teams collaborated in order to reach some consensus and develop new methods based on the best features of the old ones (ReCiPe originated from the two existing methods CML 2001 and Eco-Indicator 99) (Pizzol et al., 2011b).

Generally, the impact from any product or process (on health or ecosystems) emitted in any environmental compartment (air, water, soil) is estimated by multiplying the mass of the

contaminant emitted by a characterization factor (CF). This characterization factor is obtained by multiplying the fate factor (FF) with an effect factor (EF). FF is the fraction of substance transferred from the compartment of emission to the compartment of reception and its residence time in it (Haye et al., 2007). The effect factor (EF) is the effect of the substance on organisms as per concentration of exposure (Haye et al., 2007).

2.2.1 Fate & impact characterization modeling in LCA

Several characterization methods are currently used in LCA. Some methods as EDIP 97, make a partial evaluation with key physicochemical properties. Others, such USES-LCA and IMPACT 2002+ use multimedia models. These models generally consist of steady state first order differential equations for representing contaminant distribution between different environmental compartments (eg. Air, water, soil, sediment), degradation and advective transport. The major part of fate models were developed for environmental risk analysis of and initially to assess the fate of non-ionic organic compounds. However, some models have been developed directly for comparative methods like LCA (ex. USES-LCA and IMPACT 2002) and some models were applied to metals (eg. EUSES and CalTOX) (Bachmann, 2006; Michael Z Hauschild et al., 2008; Pennington, Margni, Ammann, & Joliet, 2005).

Some of the LCIA models take into account the spatial variability of some environmental parameters. For example, IMPACT 2002 model has a spatial version where Western Europe is divided into 135 zones. For the terrestrial environment distributed according pools 124 zones and ocean areas (each with 2 compartments and 1 water sediment compartment) and 157 zones for air divided into a grid of 2 by 2.5 degrees for air and oceans Each watershed is considered to be composed of the following compartments: soil compartment, a surface water compartment, a sediment compartment and agricultural vegetation compartment. The model assumes degradation, intermedia transfer and advection and emissions in surface water, ocean, soil and air (Godin, 2004; M. A. Huijbregts et al., 2000; Sebastien Humbert et al., 2009; Toffoletto, Bulle, Godin, Reid, & Deschênes, 2007).

The spatial version of the IMPACT 2002 model then has been adapted to the Canadian geographic context taking into account the differences between the characteristics of Canada and Europe including the population and area (Toffoletto et al., 2007).

The spatial differentiation in the LUCAS method (LCIA method Used for A Canadian-Specific context) is based on 15 Canadian ecozones and each ecozone has its own characteristics related to climate, soil, fauna, flora and human activities. The development of CF in ecotoxicity in LUCAS is currently done with a version of the IMPACT model 2002 adapted in Canadian context by integrating chemical properties of representative average environmental conditions. The IMPACT 2002 model is also the basis of IMPACT North America model which is a fate and exposure model and takes into account the geographical distribution in North America. The model was tested for benzopyrene, 2,3,7,8-TCDD and mercury (Hg) (Sebastien Humbert et al., 2009; Toffoletto et al., 2007).

The problem of using these abovementioned models with metals are, initially they were developed for organic substances, later they were made applicable to inorganics. The uncertainties due to this adaptation is quite high. Also, the documentation of assumption and calculation for most of the existing LCIA models are not very transparent. Choosing any single model which is not very well documented and then trying to make a modification within itself will pose a big challenge and introduce errors (Pizzol et al., 2011a, 2011b)

It is evident that the models vary in their scope and modeling principles, and hence also in terms of the characterization factors they generate. However, ISO has refrained from standardization of the detailed methodologies in LCA. So, with the scientific consensus of the scientists and with a careful focus on the most influential model elements, the USEtox model was established. (Dreyer, Niemann, & Hauschild, 2003; Michael Z Hauschild, 2005; Michael Z Hauschild et al., 2008; Henderson et al., 2011; Pizzol et al., 2011a, 2011b).

USEtox model is the results of scientific consensus among these model developers: CalTOX, IMPACT 2002, USES-LCA, BETR, EDIP, WATSON and EcoSense. This method performs a systematic analysis of the approaches used in analyzing the impact on the life cycle, supplementing them with a selection of environmental models not currently integrated in LCA methodologies, but with interesting features (Michael Z Hauschild et al., 2008). The development of this model was an attempt to reduce the variability of different results from different LCA models. Through this process, the inter model variation was reduced from an initial range of up to 13 orders of magnitude down to no more than two orders of magnitude for any substance (Rosenbaum et al., 2008).

The underlying four principles of the model were, that it should be parsimonious (as simple as possible, as complex as necessary), mimetic (not differing from the original models than these differ among themselves), evaluative (providing a repository of knowledge through evaluation against a broad set of existing models) and transparent (well-documented, including the reasoning for model choices). The model was kept simple and only involving the most important inter media mechanisms in order to limit the enormous amount of data requirement, since the scarcity of data is always a concern in LCA (Rosenbaum et al., 2008).

Currently, the models provide characterization factors for non-ionic and nonpolar organic compounds (as they were developed) and CF for around 18 metals although they have very strong uncertainty and were calculated only interim measure until more robust models are established (MichaelZ Hauschild et al., 2013; M. Huijbregts et al., 2010; Rosenbaum et al., 2008). Table 2-1 provides a list of metal whose CFs were generated from USEtox (freshwater ecotoxicity), IMPACT 2002+ (Terrestrial and aquatic ecotoxicity) , EUSES-LCA 2.0 and ReCiPe (freshwater aquatic ecotoxicity, marine ecotoxicity and terrestrial ecotoxicity) models.

Table 2-1 Available CFs of metals from different LCIA models

USetox (M. Huijbregts et al., 2010)	Impact 2002+ (Jolliet et al., 2003)	EUSES-LCA 2.0 & ReCiPe (Goedkoop et al., 2009)
Ag (II)	Ag	Ag
	Al	
AS (III)	As	As
AS (V)		
Ba(II)	Ba	Ba
Be(II)		Be
Cd (II)	Cd	Cd
Co(II)	Co	Co
Cr (III)	Cr	Cr (VI)
Cr (VI)		
	Cu	Cu
	Fe	
Hg (II)	Hg	Hg
Mo (VI)		
	Mn	Mn
		Mo
Ni (II)	Ni	Ni
Pb (II)	Pb	Pb
Sb (III)	Sb	Sb
Sb (V)		Sn
Sn (II)		Sr
		Ti
Ti (I)		V
V (V)		W
Zn (II)	Zn	Zn

2.3 Current LCIA modelling : The Usetox Model

The USEtox model is set up to represent a global average continent within a global box, and with an urban zone nested (the contaminants can travel from one scale to the higher scale and vice versa) within the continental box without considering any spatial differentiation of location of the emission. The continental scale consists of six environmental compartments: urban air, rural air, agricultural soil, natural soil, freshwater and coastal marine water. The global scale has the same structure as the continental scale, but without the urban air compartment. The global compartment accounts for impacts outside the continental scale and it nests the continental scale. (Rosenbaum et al., 2008). Different compartments of the USEtox model is shown in Figure 2-3.

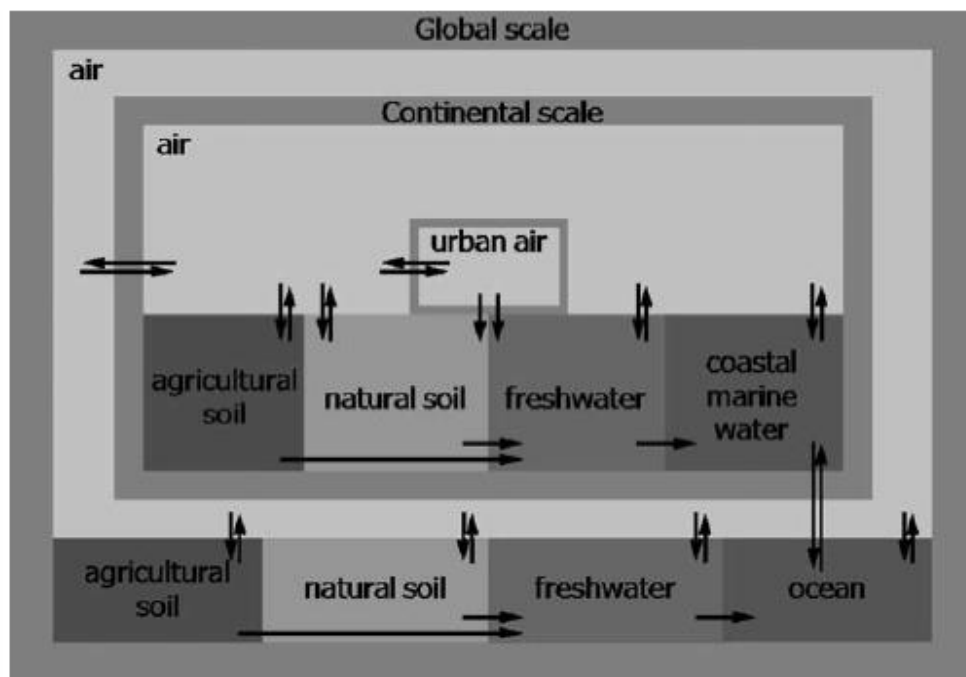


Figure 2-3 Different compartments in the USEtox model (Rosenbaum et al., 2008)

USEtox is a multi-compartment box model which calculates pollutant fate and effect to human health and ecosystem based on pollutant emission and exposure. The compartments systems and the mass flow rates are considered as homogeneous and well-mixed systems (Mackay, 2010; Rosenbaum et al., 2008).

USEtox's matrix framework is composed of a series of matrices combining fate with exposure and effect based on the matrix algebra developed by Rosenbaum, Margni, and Jolliet (2007). The links of the cause–effect chain are modelled using the matrices generated with the corresponding factors; the fate factor (\overline{FF}) in day (which also denotes the persistence of the chemical), exposure (\overline{XF}) in day^{-1} (only human toxicity) and effects (\overline{EF}) in $\text{cases/kg}_{\text{intake}}$ for human toxicity or PAF (potentially affected fraction) m^3/kg for ecotoxicity. This results in a set of scale-specific characterisation factors: (\overline{CF}) in $\text{cases/kg}_{\text{emitted}}$, as shown in Equation 2. The impact pathways related with this calculation also depicted in Figure 2-4 (Henderson et al., 2011; Rosenbaum et al., 2008).

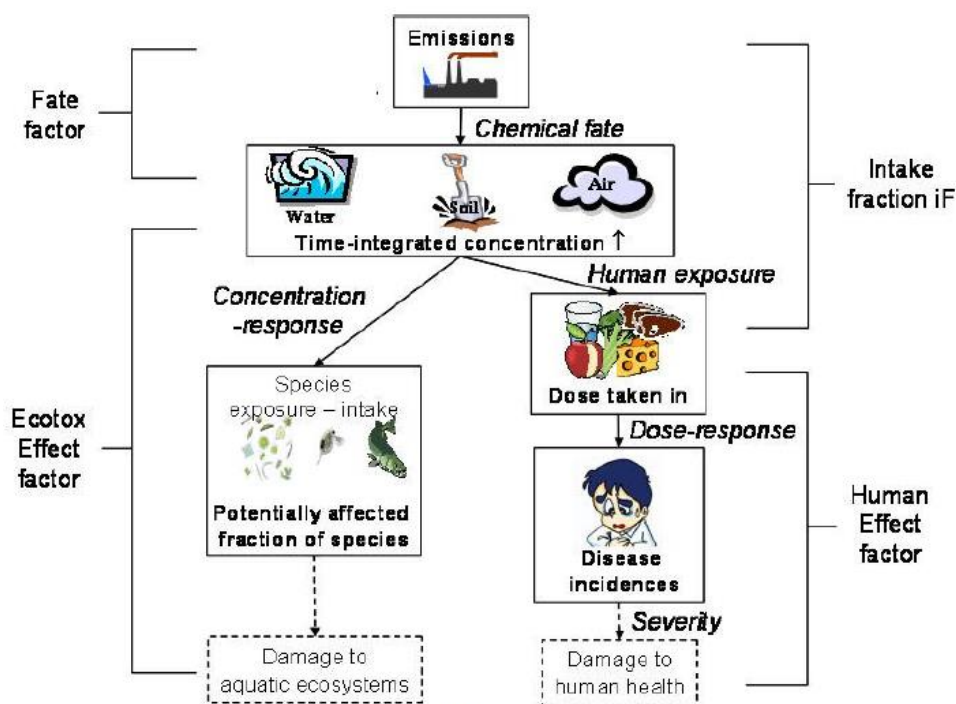


Figure 2-4 The USEtox assessment steps for the calculation of fate (Rosenbaum et al., 2008)

For ecotoxicity, the characterization factor is:

$$\overline{CF} = \overline{FF} \times \overline{EF}$$

Equation 1

For human health, after the inclusion of exposure, the expression for characterization factor becomes:

$$\overline{CF} = \overline{FF} \times \overline{XF} \times \overline{EF} = \overline{EF} \times \overline{IF}$$

Equation 2

The fate matrix (\overline{FF}) and the exposure matrix (\overline{XF}) together make the intake fraction matrix (\overline{IF}) which denotes the part of the population that are exposed to that contamination. The fate factor (FF) is same for ecotoxicity and human toxicity (Rosenbaum et al., 2008).

Characterization factors ($CF_i^{\text{freshwater ecotox}}$, [PAF m³ day/kg_{emitted}]) represent the freshwater ecotoxicological impacts of chemicals per mass unit of chemicals emitted in freshwater, where the impact is quantified as the potentially affected fraction (PAF) of species (PAF m³ day/kg_{emitted}).

For the context and brevity of this report, only the issues related to metal contamination in soil and freshwater are discussed.

The fate factor of metals are calculated in USEtox based on the total metal concentration. The CFs of metals were termed as interim (earlier) due to their relatively large uncertainties. However, in light of some recent improvements, there are new values of CF which are being added (Dong et al., 2014; Gandhi et al., 2010). Because of metals' ability to speciate in the environment, only the bioavailable form of metals are actually considered to be doing harm to the ecosystem and human health. Therefore, according to the recommendation in the Clearwater consensus in 2010 by Diamond et al. (2010), the work of Gandhi et al. (2010), Plouffe et al. (2015) Owsianiak, Rosenbaum, Huijbregts, and Hauschild (2013) and Tromson, Bulle, and Deschênes (2017) are also important to mention in this context (Diamond et al., 2010; Gandhi et al., 2010; Plouffe et al., 2015; Rosenbaum et al., 2008).

For freshwater ecotoxicity, Gandhi et al. (2010) has included the bioavailability factor (BF) for Zn, Cu & Ni for freshwater system in CF calculation using WHAM 6 as a geochemical speciation model (this model was recommended by this workshop, Diamond et al. (2010)). Later the geographic variability was also included by Gandhi, Huijbregts, et al. (2011) in a Canadian context within the calculation of CFs since metal speciation depends on the ambient environmental chemistry and regional variability to a large extent (Diamond et al., 2010; Gandhi et al., 2010; Gandhi, Huijbregts, et al., 2011).

Gandhi, Huijbregts, et al. (2011) has compared the relative ranking of Cu, Ni and Zn in 24 Canadian ecoregions. DOC, pH, hardness and water residence time were chosen the influent landscape properties for 24 Canadian ecoregions (the ecoregions and metal hazard rankings were defined by LUCAS and ChemCAN models). CFs of these metals for freshwater were by up to three orders of magnitude and it also changed the relative ranking of metal hazard between these ecoregions. FFs were varied within two orders of magnitude, BFs within two orders of magnitude for Ni and Zn and four orders of magnitude for Cu, and EFs were varied within one order of magnitude (Gandhi, Huijbregts, et al., 2011).

Dong et al. (2014) extended this approach and standardized to 14 cationic metals (Al(III), Ba, Be, Cd, Co, Cr(III), Cs, Cu(II), Fe(II), Fe(III), Mn(II), Ni, Pb, Sr and Zn) using the seven freshwater archetypes categorized by Gandhi et al. (2010). Dong et al. (2014) concluded that spatial differentiation is important for metals like Al(III), Be, Cr(III), Cu(II) and Fe(III) which form stable hydroxyl complexes in slightly alkaline waters and for them CFs varied from 2.4 to 6.5 orders of magnitude. However, for Cd, Mn, Ni and Zn which are less pH dependent and have high partition coefficients, the spatial differences are not that important since new CFs only vary between 0.7 and 0.9 orders of magnitude. For other metals, the difference is less significant (around 0.4 orders of magnitude). When compared to current CFs, most of the newly calculated CFs are similar or higher and fall within the same two orders of magnitude (Dong et al., 2014).

Plouffe et al. (2015) has attempted to include metal speciation in terrestrial ecotoxicity in the calculation of CFs. Plouffe et al. (2015) has also used WHAM 6 as geochemical speciation model for soil metal speciation to define the bioavailable factors (BF). In the work that followed (Plouffe et al., 2016), had included the geographic variability into account along with speciation. The resulting aggregated terrestrial CF (4.70 PAF.m³.day/kg) is 62 times lower than the CFs calculated

using current methodology in USEtox (292 PAF.m³.day/kg). Again, using the value for soluble Zn, the aggregated global default CF value based on true solution Zn was (1.45 PAF.m³.day/kg) 201 times lower than the USEtox derived terrestrial CF (Plouffe, Bulle, & Deschênes, 2014 (Submitted); Plouffe et al., 2015).

Henderson, Dingsheng, and Jolliet (2012) had included speciation of Al on 12 EU water archetypes by Gandhi et al. (2010) in order to verify the Ecoinvent assumption that 100% Al is leached to groundwater from landfill and then to surface water. A conceptual model was constructed from the landfill site to the surface water and finally to a water treatment plant. WHAM 6 was used to perform the speciation of Al in this study. The results of including removal of Al in groundwater leads to a reduction in the fraction of a landfill emission transferred to surface water on the order of 10⁻⁴ to 10⁻⁶. This was assumed previously as 1 (100%) (Henderson et al., 2012).

In another recent study, a different approach was tested to obtain terrestrial ecotoxicity CFs for Cu and Ni by Owsianiak et al. (2013). In this study, empirical regression was used instead of using the computer models for soil speciation. A new factor (accessibility factor) was introduced in the definition of CF, although it was not mentioned in the recommendations of Clearwater consensus. The definition of accessibility was explained as similar with the concept of risk assessment of metals, the difference being the partitioning is in the nature instead of gastrointestinal environment. Owsianiak et al. (2013) used empirical regressions on 760 soil samples to determine BFs performed on experimental field data. Soil pH, organic carbon, Mg²⁺ concentration in soil pore water and soil clay content were chosen as influential properties to affect CF. Spatial variability of 3.5 and 3 orders of magnitude were observed between CFs for Cu and Ni (two orders of magnitude in a 95% interval) (Owsianiak et al., 2013).

All of the above mentioned studies by Owsianiak et al. (2013), Gandhi, Diamond, et al. (2011); Gandhi et al. (2010); Gandhi, Huijbregts, et al. (2011) and Plouffe et al. (2015) have proven that metal speciation including spatial/regional variability into account have a big influence on the CFs of metals for both soils and freshwater ecotoxicity impact categories.

2.3.1 The soil compartment in USEtox

For the model simplicity and also to limit huge data requirement, the soil compartment in USEtox is considered as one homogeneous layer having a depth of 10 cm. Soil in reality is a complex medium consisting of several different layers. Any chemical entering in the environmental compartments are considered to be instantly in equilibrium (Rosenbaum et al., 2008).

Soil compartment was distinguished as agricultural and natural. The agricultural soil is a fraction of total soil surface. Because the ecosystem is absent in the agricultural soil it is considered as part of the technosphere. This consideration allows to account for specific (e.g. pesticides & fertilizers) emissions occurring on agricultural soil only (Rosenbaum et al., 2008).

Four mechanisms of removal were considered from soil to surface water and the resulting flow of contaminants is a net result of competition between those four mechanisms. They are: degradation, volatilization, leaching to deeper layers of soil, and runoff to surface water. For surface water, only the chemical mass dissolved in (pore) water is modeled as available for taking part in physical and chemical processes (Henderson et al., 2011).

While considering the runoff, based on typical values for a temperate climate, USEtox assumes that half of net precipitation onto soils is evaporated, with the remaining half being split equally between surface water runoff (25%) and water infiltration (25%) through soil. The latter also implies that this transfer is limited to maximum of 50% from soil to surface water. However, chemicals can also be removed from the upper soil compartment via leaching to deep soil or groundwater, which removes mobile chemicals from the upper soil compartment. (Henderson et al., 2011).

Deposition to soil and fresh water in the global box is limited, since two thirds of the area in the global box is ocean. Wet removal by intermittent rain is responsible for the high fraction transferred to soil at low K_{aw} (air-water partition coefficient). The direct transfer from air to surface water ($f_{a,w}$) also depends on K_{aw} , but deposition is limited by the fact that freshwater covers only 2.7% of the area in the continental box, and 0.9% in the global box. Therefore, the transfer from air to water is mostly via the soil compartment to water. However, Henderson et al. (2011) mentioned in the description of fate in USEtox that, this will only be important for substances with a high transfer to soil ($\log K_{aw} < -4$ and $t_{1/2(air)} > 1$ day) and a high transfer fraction from soil to water

($\log K_{oc} < 4$). As a result, only a small subset of substances has an air to surface water transfer fraction higher than 20% (Henderson et al., 2011; Rosenbaum et al., 2008).

2.4 Metals in the environment

Metals are part of the earth's crust and occur naturally in varying amounts in all environmental compartments. Metals cannot be created or destroyed. Human activities have increased the rate of redistribution of metals in the environmental compartments, particularly since the industrial revolution (Garrett, 2000). Emissions from metal mining, smelting and refining, power generation and solid-waste incinerators, manufacturing, and transportation sectors are some of the major sources of metals (Gandhi, 2011). After the emission of metals into the environmental compartments (air, water, soil, sediments) it is never decomposed or removed from the system and further they can bond with other anions and take various oxidative states having different characteristics and toxicity (speciation).

2.4.1 Metal speciation and bioavailability

Speciation is a crucial parameter for metals since it governs mobility, environmental fate, their availability to living organisms and associated toxic effects. Metal speciation includes all physicochemical forms included in the total concentration of metal in the environment (Ge, 2002). When metal is released into the soil, it can be found in the various forms: dissolved, exchangeable fraction, organic fraction, inorganic fraction, residual fraction, fraction incorporated with organic material etc. These species coexist in the environment and may or may not be in thermodynamic equilibrium (Fairbrother, Wenstel, Sappington, & Wood, 2007; Ge, 2002; N. M. Hassan, 2005).

Metal speciation may also include metal different ionic forms. Indeed, some metals and metalloids including Cr, Cu and Hg can have several degrees of ionization, which affects their mobility, fate and toxicity in the environment. For example, trivalent Cr species have low toxicity as low bioavailability, since they tend to form strong organic and inorganic complexes. In contrast, hexavalent Cr species are highly soluble and easily absorbed by living organisms, where they can result in toxic effects (carcinogenic, teratogenic and mutagenic effects) (Daulton, Little, & Lowe, 2003; Williams, James, & Roberts, 2003).

After the Clearwater consensus, the definition of bioavailability was included in the calculation of characterization factors of metals, since metals are persistent and every form of metals were not considered harmful to human health and the ecosystem. The previous assumption of the inclusion of total metal concentration in the characterization factors was overestimating the impacts (Diamond et al., 2010).

The bioavailability Factor (BF) explicitly expresses the relationship between total dissolved and bioavailable chemical where the latter is assumed to be the truly dissolved concentration of the metal that does not include colloiddally bound chemical (Diamond et al., 2010). So according to this definition, the BF can be written as:

$$BF = \frac{[Metal]_{true\ solution}}{[Metal]_{soil}}$$

Equation 3

As mentioned in section 2.3, following the Clearwater consensus and after several attempts by various groups of researchers for including speciation into the LCA modeling (Dong et al., 2014; Gandhi et al., 2010; Henderson et al., 2012; Plouffe, 2015), the uncertainty was greatly reduced and it justified the need to take metal speciation under consideration.

2.4.1.1 Factors affecting metal speciation

The parameters that are most influential in speciation of heavy metals in soils are pH, temperature, redox potential, composition and concentration of other ions, organic matter (OM), cation exchange capacity (CEC), complexing agents (Carbonates), size and quantity of soil particles and the activity of microorganisms and plants. For most metal ions, pH plays an important role since it changes the metal's solubility (aquatic & soil solution), adsorption (soil) and other parameters of influence (DOM and carbonate) for both soils and water (Sauvé, Hendershot, & Allen, 2000). At higher pH, adsorption of metals is increased and retained within the solid phase (Gandhi, 2011; Ge, 2002; Hellweg, Fischer, Hofstetter, & Hungerbühler, 2005).

Organic matter is also an important factor since it allows the formation of soluble metal complexes and can increase bioavailability of metals. Depending on other chemical parameters, it can also have opposite effects (Hellweg et al., 2005). Evidently, when most of the metal in solution is bound

to dissolved organic matter (DOM), any factor that influences solubility of organic matter will also affect metal solubility (Harter & Naidu, 1995; Sauvé et al., 2000)

Similar as in terrestrial environment, in aquatic systems, metal speciation, their bioavailability and mobility are influenced by pH, redox potential, organic complexes, and salinity (Achterberg, van den Berg, Boussemart, & Davison, 1997). Metals can form complexes with ligands from organic matter, and/or may be sorbed to suspended particulate matter (SPM) that later is transported to sediments (Carignan & Tessier, 1985). In general, pH and redox are among the most important factors that affect the mobility of sediment-bound metals in water (Wen & Allen, 1999). It is observed that lower pH increases metal dissolution (Förstner, Ahlf, Calmano, Kersten, & Salomons, 1986).

During seasonal changes when water transitions from oxic to anoxic conditions, mobility of Fe and Mn is increased due to dissolution of their oxide forms in the moderately reducing environments (Wen & Allen, 1999). Under strongly reducing conditions, metals such as Zn, Pb, Cu, and Cd are immobilized because they precipitate as metal sulphides. Conversely, these metals can be released from their metal sulphides as conditions shift from reducing to oxidizing as oxygen is introduced or during seasonal changes. (Carignan & Tessier, 1985; Hamilton-Taylor, Davison, & Morfett, 1996).

In weakly buffered sediments, a change in redox potential can change water pH, which may change the mobility of most metals (de CARVALHO, ZANARDI, BURATINI, LAMPARELLI, & MARTINS, 1998). Thus, metals deposited in sediments are not necessarily permanently immobilized. It would be safe to consider that they are rather remobilized through diagenetic processes (Carignan & Tessier, 1985) involving biological and chemical agents and by physical movement (Diamond, 1995; Förstner et al., 1986).

Metal in the soluble phase of soil can be taken up by plants where it may be stored and then returned to soil upon plant death. Metals can be transported to nearby surface aquatic systems through runoff and can also leach to groundwater thereby seemingly ‘lost’ from soils. Surface soils and groundwater could be a major source of metals to aquatic systems (Gandhi, 2011).

2.4.2 Metal speciation calculation with WHAM

WHAM (Windermere Humic Aqueous Model), is an equilibrium speciation model specifically designed to calculate equilibrium chemical speciation in environmental media. The model is

suitable especially for problems where the chemical speciation is dominated by organic matter, or the humic substances (Tipping, 1994).

According to Diamond et al. (2010), in Clearwater UNEP/SETAC workshop it was suggested to adopt the definition of BF and also to use the Windermere Humic Aqueous Model- WHAM6.0 (then available version) as a geochemical speciation model since it was commonly known and used model in that category and also considers the complexity of organic matter into account (Diamond et al., 2010; Gandhi et al., 2010; Plouffe et al., 2015).

WHAM models was developed by Tipping (1994) and it was claimed that the model was applicable for water, groundwater, soils and sediments. Plouffe et al. (2015) had been used the model assuming soil as a solution with plenty of particulate matter in it considering only soil properties listed in HWSD. Because of its reactions with organic matter content and other important metal ligands in the soil, it was possible to quantitatively input particulate matter, making it simpler to use compared to other speciation models (e.g. MINEQL+). Plouffe et al. (2015) had applied the model (WHAM 6) in soil context and validated the results with the published experimental data. Because this project will deal both soil and water, using one model for both will produce more consistent results with easier interpretation compared to using different models for different environmental compartments (Plouffe et al., 2015).

In the studies mentioned in the section 2.3, Gandhi et al. (2010), Plouffe et al. (2015) and Plouffe (2015) had used WHAM 6 in order to calculate the soil-water partition coefficient (K_d) values. The values of K_d was calculated by dividing the particle bound Zn concentration to the total aqueous Zn concentration values (Equation 4) from WHAM results (Gandhi et al., 2010; Plouffe, 2015):

$$K_d = \frac{[Metal]_{particle\ bound}}{[Metal]_{total\ aqueous}}$$

Equation 4

Currently, the latest available version for this speciation model is WHAM 7. It offers expanded database for cation binding to humic and fulvic acids, capability to calculate the effect of

uncertainty in input variables and model parameters on model outputs and ability to run sets of multiple input files automatically. Some improvements in the quartz and silica database were also performed in this new version (CEH-UK, 2014; Lofts, 2012).

2.4.3 Essential metals

Certain metals (Fe, Mn, Cu, Cr, Co, Zn, Cd) are essential for optimum human health. They are required for humans, animals and other organisms in low dosage for growth, enzyme activity, sleep and other bodily functions. Deficit in them will create adverse effects. On the other hand, excess consumption and exposure of these metals can also cause adverse effects. Other metals such as Hg, Pb, Cd, Al are toxic regardless of their concentrations beyond their threshold values. These toxicity thresholds should be considered in the determination of effects of metals on living organisms and on the ecosystems (Basta, Ryan, & Chaney, 2005; Landner & Reuther, 2005; Plouffe, 2015).

2.4.3.1 Essentiality of Zn

Like other metals, Zn is naturally occurring and it is a nutritionally essential element. Trace amounts are required for the basic cellular function of all living things for various structural, regulatory and catalytic biological processes. Zn-binding motifs, common structural protein domains found in ~10% of all proteins play critical roles in numerous cellular processes including protein folding, enzymatic activity, immune function, macromolecule syntheses, DNA repair and oxidative stress responses. Zn is not endogenously produced and must be obtained through diet. Humans consume Zn from variety of foods such as meat, seafood, dairy products, beans and whole grains and dietary supplementations (Guynn & Chan, 2017).

2.4.3.2 Zn distribution in Soil and water

In nature, Zn is found in many forms. In the (soil) solution, Zn can be found as: Zn^{2+} , ZnCl^+ , ZnOH^+ , ZnHCO_3^+ , ZnO_2^{2-} , Zn(OH)_3^- , ZnCl_3^- ions. Most common and available solid forms are: ZnCl_2 , ZnO , ZnSO_4 and ZnS (Kabata-Pendias, 2010). Different studies reported a variety of distribution in Zn (K_d values) found in soils. In Stephan et al. (2008) work, the partition coefficient value for Zn ranged from 17 to $1.3\text{E}+05$ L/Kg (Stephan et al., 2008). Nolan, McLaughlin, and Mason (2003) had reported their K_d value varied between $1.24\text{E}+03$ to $9.18\text{E}+04$ L/Kg (Nolan et

al., 2003). For freshwater, Zn is well distributed among the solid and solution phase since the environment is less heterogeneous than in terrestrial system. The K_d value varied over 1 order magnitude for Zn ($\log K_d$ 4.4 to 5.4 L/Kg) for European water (Gandhi et al., 2010). Similarly, also in the study by Dong et al. (2014) the calculated K_{ds} for suspended solids and colloidal Zn varied over 1 order of magnitude (Dong et al., 2014).

2.5 Flow of water & solutes through Soil

It was considered in USETox that a portion of the contaminant leaches to deeper layers of soil. However, the soil compartment in this model is only 10 cm deep and it is considered as a homogeneous layer. What happens after the contaminant is leaching or infiltrating (as per the written explanation inside the USETox model) through soil is not mentioned. Given that, the infiltration process is considered as a removal mechanism from the soil compartment and the contaminant might degrade over time but this assumption cannot be realistic for metals. Metals do not undergo degradation, they might stay in the soil layers being accumulated over time, and move downward contaminating groundwater when soil sorption capacity is exceeded.

In reality, the great heterogeneity of all soil types would lead us to no uniform results, although useful correlation might be made in individual soil types and layers. According to Bowen (1979), the nature of most soils is shown by a series of layers of different colors and textures when a trench is dug. The upper layer, containing more or less decomposed plant debris, is called A layer. Below this, is the B layer, which consists of rock fragments more or less completely weathered to clays and hydrous oxides, mixed with organic matter. Below this again is the C layer of subsoil or parent rock (Bowen, 1979).

There are mainly two types of flow through the soil. The preferential flow, which refers to the uneven and rapid movement of water and solutes through porous soil, characterized by regions of enhanced flux through such as wormholes, root holes, cracks etc. And, the matrix flow, which is relatively slow and even movement of water and solutes through the soil. As reported by Lennartz and Kamra (1998), from different laboratory analysis experiments performed with soil coring, extraction of the soil solution and by suction of soil solution samplers showed that, the preferential flow is a dominant process for solute mobility when compared with the soil matrix flow regime

(Cornell_BEE, 2014; Lennartz & Kamra, 1998; Roth, Jury, Flühler, & Attinger, 1991; Van Wesenbeeck & Kachanoski, 1991; Ward, Kachanoski, Von Bertoldi, & Elrick, 1995).

The transfer of contaminants in the soil depends on physicochemical properties of the soil and the substance. The infiltration capacity of a soil determines whether and how much of the water can seep into the deeper soil layer. Generally in soil, preferential (macropore) flow and sorption (matrix flow) are two main types of transfer processes. The fraction of macropore flow in soils can be high reaching up to more than 90% of the total flow. It is often difficult to estimate the fractions of water that are subjected to macropore flow, interrupted macropore flow, since according to Iqbal (1999), rain events and macropore channel geometry can change their flow behavior. They also in-homogeneously flow through the soil matrix. Diffusion through the macropore channels are very small compared to other mode of transport. Again, the number of continuous macropores in soils varies in time and space (Bergström & Shirmohammadi, 1999; Hellweg et al., 2005; Iqbal, 1999).

The residence time of the contaminants depends on the soil texture (sand, clay, silt). Bowen (1979) and Oostindie and Bronswijk (1995) had conducted experiments with clay type soils for water residence time and stated that saturated clay has low hydraulic conductivity. The vertical residence time of water flowing through saturated clay layers is longer as reported by Oostindie and Bronswijk (1995). Because of these longer residence times and the high adsorption capacity of clay, contaminants will often be adsorbed. They can also be transformed by chemical or microbiological processes, before passing through a clay layer. Therefore, clay soils overlying an aquifer effectively protect that aquifer against contamination originating from the soil's surface layers (Bowen, 1979; Oostindie & Bronswijk, 1995).

However, Oostindie and Bronswijk (1995) also mentioned, when saturated clay soils dry, their volume decreases as results of the surface's subsidence and the appearance of shrinkage cracks. Water and solutes can be transported rapidly to the subsoil and reach the groundwater by preferential flow via these cracks. In shallow aquifers, preferential flow in a cracked clay soil may lead to very short vertical residence times for solutes from the soil surface to the aquifer. Apart from the cracks in the clay type soil, the residence time is also affected by surplus precipitation, precipitation intensity, drainage, upward and downward seepage to or from the aquifer and the thickness of the layer (Oostindie & Bronswijk, 1995).

In another study, Bergström and Shirmohammadi (1999) had used dye tracer to measure the areal extent of preferential flow in sandy and clayey soils. Results of this study showed that structured clay soils, such as Lanna clay, promote bypass flow that results in fast leaching of water and solutes, whereas in sand-textured soils, such as Mellby sand, ‘piston flow’ is responsible for the flow of water and solutes. Despite lower infiltration rates in the clay than in the sand, arrival of the dye tracer at the percolation boundary was very fast in the clay soil (Bergström & Shirmohammadi, 1999).

In the same study, the reduction of stained cross-sectional areas in both soils indicated there were less macropores as they go deeper and it was more drastic for clayey soils than in sandy soils. The results also indicated the need to consider preferential flow and bimodal transport in the models which considers solute transport from soil to groundwater (Bergström & Shirmohammadi, 1999).

Koestel, Moeys, and Jarvis (2012) had conducted experiments with clayey and sandy soils to measure preferential flow and found that, preferential solute transport was shown to depend on soil texture in a threshold-like manner: moderate to strong preferential transport was only found in soils with a texture consisting of more than 8 to 9% clay. As reported, in this experiment, columns filled with glass beads, clean sands, or sieved soil exhibited no preferential transport (Koestel et al., 2012).

Some important features of macropore flow which as described by Hellweg et al. (2005), are dependent on soil texture and other spatial parameters are listed in Table 2-2. The extent and percentage of macropore flow compared to the total flow in silty and clayey soils are shown in Table 2-3 which is also adapted from Hellweg et al. (2005) which is an important source of information (Hellweg et al., 2005).

Table 2-2 Dependency of macropore flow on soil properties: adopted from (Hellweg et al., 2005)

Soil properties	Temporal variability	Explanation
Soil texture (grain size)	Small	Macropore flow is largest for finest textured medium; which means, for clayey soils, macropore flow will be higher than in sandy soils. The order will be clay>silty>sandy (Booltink & Bouma, 1993; Ghodrati, Chendorain, & Chang, 1999; Li & Ghodrati, 1997).
Depth in soil	Small	The number of continuous macropores decreases with depth. Since the macropores are structural cracks, worm holes or root channels, the absence of them in the deeper layers decrease the flow (Bergström & Shirmohammadi, 1999).
Thickness of the soil layer	Small	Thin soil layers have more macropores. So with the increasing thickness, the flow reduces (Oostindie & Bronswijk, 1995).
Soil and infiltration rate	High	<p>Macropore flow might increase with soil moisture and rain intensity (Iqbal, 1999; Li & Ghodrati, 1997). For instance, infiltration into dry soil might fill up voids in the matrix first. When the infiltration capacity of the soil matrix is exceeded, water passes to the macropores (Bouma & Dekker, 1978). Moreover, macropore channels have variable width and continuity depending on rain intensities and water saturation. High infiltration rates and ponding increase the continuity of macropores by activating laterally interconnecting macropores (Iqbal, 1999).</p> <p>However, in dry soils, shrinkage cracks can also contribute by increasing the macropore flow (J. J. B. Bronswijk, 1988).</p>

Table 2-3 Fraction of macropore flow compared to the total flow in silty and clayey soils adopted from: (Hellweg et al., 2005)

Soil type	Soil texture and composition	Depth/thickness	Fraction of macropore flow	Reference
Silty soil	8-18% sand, 47-74% silt, 18-35% clay	50 cm	32-43%	(Hellweg et al., 2005)
	Silty loam	35 cm	40-50%	(Germann, Edwards, & Owens, 1984)
	Fine-silty, mixed, (36% silt, 31% clay)	20 cm	45% @h=-10m 70% @h=-2m	(Camobreco, Richards, Steenhuis, Peverly, & McBride, 1996)
	Sandy loam (24-26% sand, 55-56% silt, 15-20% clay)	1 m	More than 99%	(Van Stiphout, Van Lanen, Boersma, & Bouma, 1987)
Clayey soil	Light to medium-heavy clay (31-44% clay content)	1m	41%	(Jorgensen P et al., 1998)
	Clay (often >50% smectites)	43 cm	35%	(Hendriks, Oostindie, & Hamminga, 1999)
	Very fine clayey, mixed illitic-emontmorillonitic, mesic typic Fluvaquent (52-69% <2 μ mm)	0.77 cm (tile drains)	0-80%, depending on rain intensity and soil moisture	(Wilkison & Blevins, 1999)
	Heavy clay soil	1.8 m	30-40%	(J. J. B. Bronswijk, 1988)
	Very fine clayey, mixed illitic-montmorillonitic, mesic typic Fluvaquent (51-60% clay)	1.2-1.4 m (tile drain)	Large fraction, under dry soil conditions all transport	(Oostindie & Bronswijk, 1995)
	Clay loam (25-35% clay) and clay (50-100% clay)	20 cm	64% (clay loam), 79% (clay)	(J. Bronswijk, Hamminga, & Oostindie, 1995)

Again, adsorption, complexation, and precipitation also influence the speed of metal transport in soils. These processes again depend on spatially variable parameters and on the speciation of the metals. The speciation of metals varies with both spatial parameters, geographic conditions and also on the background concentration of the metal (Hellweg et al., 2005).

Adsorption of metal on soil also depends on available surface sites. The preferential adsorption of heavy metals strongly depends on the metal concentration and the type of interaction with the solid surface. Some heavy metal cations like Cu^{2+} and Pb^{2+} may form complexes with dissolved organic acids in the soil. Whether the subsoil can retain these organic complexes depends on the content of organic matter. Dissolved organic complexes have been observed to directly penetrate to the groundwater. In soils, where there is higher percentage of calcite, (pH of the soil is neutral to basic), the anions are observed to directly penetrate to groundwater. The mobility of organic metal complexes are generally limited in soils (Hellweg et al., 2005).

In case of higher pH value of soils, the specific adsorption of the metals increases and the mobility of metals are reduced. This is true for Cd^{2+} , Ni^{2+} , Cu^{2+} and Pb^{2+} since they form hydroxo complexes, which adsorb to sesqui-oxides. The presence of other heavy metals might influence the mobility of metals in soil. Hellweg et al. (2005) claims that Cd^{2+} mobility can be enhanced by high concentration of Pb^{2+} (Hellweg et al., 2005).

2.6 Groundwater and its hydraulic properties

Groundwater represents one portion of the earth's water circulatory system known as the hydrologic cycle. It constitutes 0.39% of the world's water but 49% of the world's freshwater. Water-bearing formations of the earth's crust act as conduits for transmission and as reservoirs for storage of water. Water enters in these formations from natural recharges such as, precipitation, streamflow, lakes and reservoirs and travels slowly for varying distances until it returns to the surface by action of natural flow, plants or humans (Aral & Taylor, 2011; "Groundwater Hydrology," ; Todd & Mays, 2005).

Above the water table, the saturation begins to decrease as the elevation increases. The subsurface occurrence of groundwater may be divided into two zones: the aeration zone and the saturation zone. The zone of aeration consists of interstices occupied partially by water and air. This zone

can be further sub-divided into soil water zone, the intermediate vadose zone and the capillary zone. The water in this zone is under tension, it is held by capillarity and exhibits a fluid pressure that is below the atmospheric pressure. Here, the saturation remains high, sometimes 100%. The saturated zone extends from the upper surface of saturation down to underlying impermeable rock. Water in saturated zone always has higher pressure than the atmospheric pressure (Aral & Taylor, 2011; Todd & Mays, 2005).

The water level in a well usually expresses as height over sea level, is the total head (ht), which consists of elevation head (z) and pressure head (hp);

$$ht (m) = z (m) + hp (m)$$

Equation 5

In an unconfined aquifer, pressure head (hp) equals zero at the water table surface because it marks the transition from negative pressure head in the vadose zone to a pressure head that may be either negative or positive in the saturated zone. In a ground water recharge zone, the pressure head decreases with increasing depth, whereas in a discharge zone, the pressure head increases with depth (Boulding & Ginn, 2003).

The hydraulic gradient is measured as the change in water level per unit of distance along the direction of maximum head decrease. It is determined by measuring the water level in several wells that measure the true unconfined water table or the same confined aquifer. The hydraulic gradient is the driving force that causes groundwater to move in the direction of decreasing total head (Boulding & Ginn, 2003).

Aquifers are classified as unconfined where the top of the saturated zone is at atmospheric pressure, and confined, where a slowly permeable geologic layer prevents upward flow when the hydraulic head is above the level of confining layer, causing pressure head at the top of the aquifer to exceed atmospheric pressure. Confined aquifers are classified as either semi-confined or leaky and confined aquifers according to their permeability of the confining layers. The term ‘highly confined’ is used in case of the confining layer’s very low permeability (since, no confining layer is completely impermeable). Unconfined water table are of two types, perched or regional. Perched water table rests on impermeable strata, there is unsaturated flow below. In regional aquifers, all

waters move by saturated flow until it reaches to a point of surface discharge (Boulding & Ginn, 2003).

Naturally, groundwater is invariably moving. This movement is governed by established hydraulic principles. Flow through the aquifers can be expressed by hydraulic conductivity or Darcy's law. Experiments show that the applications of Darcy's law enable groundwater flow rates and directions to be evaluated. This law is valid for $N_R < 1$ to $N_R = 10$. Fortunately, most natural underground flow occurs with $N_R < 1$, so Darcy's law can be applicable. Groundwater movement and flow rates are obtained using the hydraulic conductivity and the hydraulic gradient. Groundwater velocities vary widely depending on local hydrogeologic conditions; values from 2m/yr to 2km/yr are normal. Usually, velocities tend to decrease as the depth increases since porosity and permeability decrease (Todd & Mays, 2005).

Todd and Mays (2005) had listed the representative values of hydraulic conductivities for different types of soil textures which were adopted from Morris and Johnson (1967), are presented in Table 2-4.

Table 2-4 Representative values of hydraulic conductivity. Source: Morris and Johnson (1967), Todd and Mays (2005)

* R stands for repacked sample; H & V stands for horizontal and vertical conductivity respectively.

Material	Hydraulic conductivity (m/day)	Type of measurement
Gravel, coarse	150	R
Gravel, medium	270	R
Gravel, fine	450	R
Sand, coarse	45	R
Sand, medium	12	R
Sand, fine	2.5	R
Silt	0.08	H
Clay	0.0002	H
Sandstone, fine-grained	0.2	V
Sandstone, medium-grained	3.1	V
Limestone	0.94	V
Dolomite	0.001	V
Dune sand	20	V
Loess	0.08	V
Peat	5.7	V
Schist	0.2	V
Slate	0.00008	V
Till, predominantly sand	0.49	R
Till, predominantly gravel	30	R
Tuff	0.2	V
Basalt	0.01	V
Gabbro, weathered	0.2	V
Granite, weathered	1.4	V

2.6.1 Transport processes through Groundwater compartment

The mass conservation system for a dissolved species (considering metal and metal complexes are dissolved in water) in a groundwater system is (*Equation 6*):

$$\left(\begin{array}{c} \text{Net rate of change} \\ \text{of solute mass} \\ \text{withing the system} \end{array} \right) = \left(\begin{array}{c} \text{Flux of solute out} \\ \text{of the system} \end{array} \right) - \left(\begin{array}{c} \text{Flux of solute} \\ \text{into the system} \end{array} \right) + \left(\begin{array}{c} \text{Loss or gain} \\ \text{of solute} \\ \text{mass due to} \\ \text{reactions} \end{array} \right)$$

Equation 6

The physical processes that control the contaminant flux into and out of the groundwater system are advection, mechanical dispersion and molecular diffusion. Other processes also include loss and gain of contaminant mass in the system which are: biological and radiological reactions.

Advection: As defined by Fetter and Fetter Jr (1999), transport by advection is the movement of contaminants by the flowing groundwater. Contaminants travel at a rate equal to the average linear velocity of the groundwater. Mathematically, the advective flux is expressed by *Equation 7* under the assumption that contaminant mass does not alter the water density sufficiently to impact the groundwater flow pattern (Aral & Taylor, 2011; Fetter & Fetter Jr, 1999).

$$J = v n_e C$$

Equation 7

Where **J** is the advective mass flux [ML⁻²T⁻¹]

v is the average linear velocity of groundwater [LT⁻¹]

n_e is the effective porosity through which flow occurs

C is the concentration of the contaminant [ML⁻³]

The average linear velocity v can be determined from the following equation (Fetter & Fetter, 2001):

$$v = -\frac{K}{n_e} \cdot \frac{dh}{dl}$$

Equation 8

Where, K is the hydraulic conductivity [LT^{-1}] and dh/dl is the hydraulic gradient.

The product of average linear velocity and time elapsed since contaminants were introduced into groundwater system defined the position of the advective front. This is defined as a sharp front by Fetter and Fetter Jr (1999), where the concentration of the contaminant behind the front is of the moving groundwater while on the other side it is the background value (Fetter & Fetter Jr, 1999).

Diffusion: According to Fick's law, in a one dimensional flow system, in the direction to the decreasing concentration the diffusive mass flux F would be:

$$F = D_d \frac{dC}{dl}$$

Equation 9

Here, F is the diffusive mass flux [ML^2T^{-1}]

D_d is the diffusion co-efficient for open water [L^2T^{-1}]

C is the contaminant concentration [ML^{-3}]

$\frac{dC}{dl}$ is the concentration gradient [ML^{-4}]

In situations where the concentration changes with time, Fick's second law can be applied. In a one dimensional system, where contaminant transport is by molecular diffusion only, Fick's second law is given by Equation 10.

$$\frac{\partial C}{\partial t} = -D_d \frac{\partial^2 C}{\partial x^2}$$

Equation 10

Where, $\frac{\partial C}{\partial t}$ is the rate of change of concentration [$ML^{-3}T^{-1}$]

Equation 10 considers molecular diffusion at a microscopic scale. In the subsurface, diffusion occurs within the porous medium and molecular diffusion is constrained relative to that of open water. To represent molecular diffusion in porous media (macroscopic scale), an effective diffusion coefficient D^* is proposed by Ingebritsen and Sanford (1999), which is presented in Equation 11 (Ingebritsen & Sanford, 1999).

$$D^* = \frac{n_e}{\tau} D_d$$

Equation 11

τ is the totuosity which is defined as the ratio of the actual length of the flow path of the diffused contaminants over the straight line distance (Aral & Taylor, 2011; Ingebritsen & Sanford, 1999).

Mechanical dispersion or dilution: Dispersion is the gradual spreading of contaminants beyond the region they are expected to occupy when considering advection alone. According to Fetter and Fetter (2001), since (i) the velocity of groundwater flow being higher in center of pores than at the edges, (ii) the contaminants can pass through different flow paths to reach the same location and (iii) groundwater moves faster in larger pores than in smaller pores, the contaminants get diluted mixing with the un-contaminated groundwater. If the mixing is along the flow path it is termed as mechanical dispersion or longitudinal dispersion. The groundwater flow path may also diverge at the pore scale, where the contaminants will spread in the direction normal to the flow path, which is called lateral or transverse dispersion (Aral & Taylor, 2011; Fetter & Fetter, 2001).

Molecular diffusion and mechanical dispersion contribute jointly to the dispersive process of contamination transport. They are combined together to define a quantity called coefficient of hydrodynamic dispersion ($a_L v_i$ and $a_T v_i$) as defined by Fetter and Fetter Jr (1999) in the latter two equations:

$$D_L = a_L v_i + D^*$$

Equation 12

$$D_T = a_T v_i + D^*$$

Equation 13

Where,

D_L and D_T are the longitudinal and transverse hydrodynamic dispersion coefficients, respectively

a_L and $a_T v_i$ are the longitudinal and transverse dispersivities, respectively
 v_i is the average linear velocity in the i direction [LT^{-1}]

According to Gelhar, Welty, and Rehfeldt (1992), from averaging the published data, the value of a_L can be approximated as:

$$a_L = 0.01 L$$

Equation 14

Here, L is length of the flow path (m). Again, for lengths less than 3500m, according to Neuman (1990), a_L is defined as (Neuman, 1990):

$$a_L = 0.0175 L^{1.46}$$

Equation 15

For transverse dispersivity, a_T is typically 1/10 to 1/100 of the longitudinal dispersivity a_L . Xu and Eckstein (1995) had performed statistical analysis relating reliable dispersivity data with field scale and developed the following relationship between a_L and L (Xu & Eckstein, 1995):

$$a_L = 0.83 (\log L)^{2.414}$$

Equation 16

Chemical and biological reactions: The metals will undergo speciation and complexation reactions, which will be taken into consideration in the next objective and are discussed in detail a little later. However, the reactions involving kinetics and dynamic aspects are out of the scope of this project.

CHAPTER 3 PROBLEM IDENTIFICATION, RESEARCH HYPOTHESIS, OBJECTIVES AND METHODOLOGY

3.1 Problem Identification

The purpose of the multimedia environmental modeling is to be able to know what is happening in other environmental compartments if we emit in any compartment. USEtox is now a recommended method by UNEP/SETAC life cycle initiative for LCIA modeling on human and eco-toxicity impact categories. The number of metals included in this model is significant, (18 metals) and CFs are given consistently for each emission compartment. (Pizzol et al., 2011a).

Although USEtox is very robust and offers reliable results compared to other LCIA methods, the model made some debatable assumptions in the soil compartment. The soil compartment is considered as a sink. The ultimate destination of the metals/contaminants is not clearly addressed within this model. Whereas, in reality, some metals may propagate from soil to groundwater travelling through the deeper soil layers. Both the deeper soil layer and groundwater compartments are overlooked in the USEtox model. In Nature, most of the aquifers and groundwater table are connected to the freshwater supply and they are getting recharged on regular basis. By not considering the fate of metal in soil and groundwater we are both overestimating the fate of metals in the soil (which appears as the ultimate compartment where most of the metal emitted to soil “disappears”) and underestimating the fate of metal to surface water (as metals reaching the groundwater never potentially reaches surface water).

One of the challenges for metals in multimedia modeling is, metals speciate in the environment. Not all of the chemical forms of metals are bioavailable hence are not hazardous for humans and the environment. Following the recommendations of the Clearwater consensus attempts had been made (discussed in section 2.3 and 2.4) for the inclusion metal speciation within the LCA framework to address the fraction of metal which is responsible to have detrimental effect on human health and ecosystem (BF). Again, the dissolved fraction (not absorbed) of the metal in the soil will eventually propagate from vadose zone to the subsoil and eventually end up in surface water. Therefore, to calculate fate of metals, it is also important to address this issue along with the consideration of speciation of metals (Diamond et al., 2010).

Again, the speciation of metals depends on ambient chemistry and environmental conditions. Therefore, the USEtox model should be modified with the inclusion of subsoil and groundwater compartment along with metal speciation and geographic variability being taken into consideration.

3.2 Research Hypothesis

Not considering the link between soil, groundwater and surface water for metal emissions to soil in an LCA context is leading to an underestimation of the impact for the aquatic ecotoxicity and human toxicity impacts categories of those emissions.

3.3 Objectives

The main goal of this project is:

Construction of a fate model within the scope of LCIA (based on the USEtox model) including deeper soil layer(s) and groundwater compartments in order to model the fate of metals in these compartments and in the environment considering both spatial variability and metal speciation and linking the soil compartments with freshwater.

The goal can be further subdivided into three main objectives:

1. To construct a fate model considering all possible and important mechanisms of inter-media transfer between all soil layers (Topsoil and deeper soil layer(s)), groundwater and surface water.
2. To investigate of the fate of metals in these compartments (soil layers, groundwater) including metal speciation and spatial/geographical variability.
3. To compare the results obtained with the proposed model and with the current version of USEtox.

3.3.1 Choice of Metal : Zn

Zn was chosen because despite of being a trace metal in earth's crust it can lead to toxic effects when it is found in the environment in excess. At lower pH, free Zn is very soluble and mobile

divalent trace cations and therefore often one of the most phytotoxic traces after free Al and Mn. Zn is used in industries as protective coating against corrosion, as a catalyst in various chemical processes (eg rubber, pigments, plastics, lubricants and pesticides), in batteries, automotive equipment, etc. Some Zn compounds even have dental and medical applications (Kabata-Pendias, 2010). Thus, it is important to better evaluate its ecotoxicological impacts. Zn is also a major contributor to the average Canadian's ecological footprint primarily in relation to terrestrial ecotoxicity (Lautier et al., 2010). In addition, according to Pizzol et al. (2011a) the contribution of Zn to ecotoxicity is highly variable according to the chosen LCA methods (Pizzol et al., 2011a). Further study on Zn therefore becomes crucial in determining its actual contribution.

3.4 General methodology

The first step is to determine the soil/water partitioning coefficients (K_d) for Zn in soil and in subsoil using the WHAM7 speciation software for all the different soil and subsoil units from the harmonized world soil database (HWSD v.1.2) are calculated.

In the second step, considering all the soluble Zn fraction from soil is mobile, the bioavailable fraction for freshwater ecosystems is calculated, as recommended by the Clearwater consensus (and as already operationalized by Gandhi et al. (2010) and Dong et al. (2014)) using the freshwater properties in the different watersheds (basins and sub-basins) around the world. For freshwater, K_{pss} and K_{DOC} are calculated using WHAM7 and aquatic effect factors (EF) are calculated with BLM from the water properties available from different databases (GEMStat, EuroGeoSurveys, etc).

The third step Watershed specific K_d s were calculated by intersecting the soil and watershed map layers in GIS.

In the fourth step, a modified version of USEtox is created in which the groundwater compartment is connected to the soil and to the surface water compartments. For each native resolution cell, the fate and characterization factor of Zn is calculated by considering that Zn has different properties in each cell (ie the soil and subsoil specific K_d s in soil and groundwater compartment respectively and the receiving watershed specific K_{pss} , K_{doc} , BF and EF).

Lastly, the results obtained at the native resolution scale are aggregated at different more operational regionalization scales: watershed, country, continent and global level. The corresponding spatial

variability due to aggregation at a coarser scale is determined. The results are compared to the default values of USETox.

CHAPTER 4 ARTICLE 1: REGIONALIZED AQUATIC ECOTOXICITY CHARACTERIZATION FACTOR FOR ZINC EMITTED TO SOIL ACCOUNTING FOR SPECIATION AND FOR THE TRANSFER THROUGH GROUNDWATER

This manuscript of the article presented here has been submitted to the International Journal of Life Cycle Assessment (JLCA). In this study USETox model is modified by connecting the soil and freshwater compartment via subsoil & groundwater. The fate and characterization factors are calculated with the modified USEtox and also with the inclusion of metal speciation. The selected metal for our study is chosen as Zn. The results are compared with the original version of USETox. The study is supervised by Mme Louise Deschênes, Professeure et co-titulaire de la Chaire ICV, Polytechnique Montréal (génie chimique) and Mme Cécile Bulle, Professeure, ESG UQÀM.

4.1 Regionalized aquatic ecotoxicity characterization factor for Zn emitted to soil accounting for speciation and for the transfer through groundwater

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4.2 Abstract

4.2.1 Purpose

The goal of this study is to calculate regionalized fate and characterization factors for Zinc (Zn) emitted to soil considering the Zn transfer through groundwater in USETox and Zn speciation in soil, groundwater and surface water using regionalized soil, subsoil and freshwater parameters.

4.2.2 Methods

First, the soil/water partitioning coefficients (K_d) for Zn in soil and subsoil and suspended solid-water partition coefficient, organic carbon-water partition coefficient, bioavailability and effect factors for freshwater are calculated using WHAM7 software. Second, soil and watershed maps are intersected with geographic information system obtaining some geographical cells (native resolution cells). Third, USETox is modified by linking a) the soil with subsoil & groundwater compartment and b) subsoil & groundwater compartment to the freshwater compartment. Soil to water fate factors (FF_{sw}) for each native resolution cell are calculated using these soil, subsoil and watershed partition coefficients in the modified version of USETox. These specific FF_{sw} s are multiplied with bioavailability factors (BF) and effect factors (EF) to generate characterization factors (CF_{sw}) for all the native resolution cells. Fourth, the results obtained at the native resolution scale are aggregated at different more operational regionalization scales: country, continent and global level, with the corresponding spatial variability determination. Lastly, the results are compared to the default values of USETox.

4.2.3 Results and Discussion

Regionalized freshwater ecotoxicity characterization factors for Zn emitted to soil have a global spatial variability over 3 orders of magnitude. The weighted average global value is in the same order of magnitude with the default USETox value (1.48 times lower). The spatial variability of the Zn soil to water fate factors (FF_{sw}) and of the characterization factors (CF_{sw}) within each watershed is quantified. The results are illustrated on a world map for all the native resolution cells. With the exception of Europe, all the regional and continental FF_{sw} and CF_{sw} varied over 2 orders magnitude.

4.2.4 Conclusions

The inclusion of the transfer through groundwater of the Zn soil emissions in fate and in characterization, along with the Zn speciation, allows better predicting the potential impacts from soil metal emissions. The spatial variability of Zn CF_{sw}s at continental scale is close to the uncertainty of USEtox CFs (two orders of magnitude), meaning that using a continental level CF seems a reasonable compromise between a too intensive data collection and a too imprecise impact assessment.

4.2.5 Keywords

Freshwater ecotoxicity, Metal speciation, LCIA, Zn, Subsoil, Groundwater, Characterization Factors

4.3 Introduction

The aim of the present study is to propose an approach to calculate the fate factors (FFs) and the freshwater ecotoxicity characterization factors (CFs) of metals emitted to soil accounting for the metal speciation and for the metal transfer to freshwater through groundwater using an adapted version of USEtox.

USEtox is a consensual life cycle impact assessment (LCIA) model developed within the UNEP-SETAC Life Cycle Initiative allowing to calculate CFs (ie the quantity of environmental impact per quantity of substance emitted) for human toxicity and ecotoxicity (Rosenbaum et al., 2008). Metal ecotoxicity is considered as poorly modeled by USEtox. During the Clearwater consensus, the need to account for metal speciation has been identified as one of the key priorities by a group of experts to improve the ecotoxicity impact assessment of metals in LCA (Diamond et al., 2010). The movement and exchanges of a contaminant in soil and water interface is governed, among other properties, by its partitioning coefficients giving the partition between solid and water (in soil, subsoil and water compartments). In the case of metals, different species of metal are co-existing, some being soluble in water, other not, hence metal solid-water partitioning coefficient depend on metal speciation. Moreover, the metal speciation depends on the physico-chemical properties of the environmental media in which the metal is. Recent developments were done to consider metal

speciation in freshwater and terrestrial ecotoxicity. Gandhi et al. (2010) have used WHAM6 speciation model to include metal speciation in aquatic environment to determine the freshwater ecotoxicity CFs for Cu, Ni, Co, Cd and Pb for seven European freshwater archetypes. The resulting CFs are 1 to 4 order of magnitude lower than the CFs without accounting for speciation (Diamond et al., 2010; Gandhi, Diamond, et al., 2011; Gandhi et al., 2010). Dong et al. (2014) generalized the same methodology and applied it to all the other metals available in WHAM. The resulting site-specific CFs were similar or slightly higher than the generic CF of USEtox for Cd, Co, Ni, Pb and Zn, but 1-2 orders of magnitude higher for Cu. Interestingly, according to Dong et al. (2014) site chemistry did not affect much Cd, Mn, Ni and Zn results; their CFs varied only 0.7-0.9 order of magnitude across archetypes. These metals have shown the highest CF where the water had the lowest DOC concentrations, allowing to conclude that these metals have affinity to organic ligands, which presence was therefore reducing their bioavailability to the biota/environment (Dong et al., 2014). Plouffe et al. (2016) have calculated the terrestrial ecotoxicity CFs also using WHAM6 for all the soil units from the harmonized world soil database (HWSD). CFs spread over 14 orders of magnitude for the world and the global CF is 50 times lower than the generic USETox CF when considering the true solution of Zn as being the bioavailable one – which corresponds to the Clearwater consensus recommendation but does not allow any robust validation of the WHAM model parameterization in soil given the lack of field measurement of the true soluble fraction of metal in the literature; When considering that the soluble fraction is the bioavailable one, which is less in agreement with the Clearwater consensus recommendation, but allows a better validation of the WHAM speciation model as several hundreds of soil samples from all around the world with measured values of the soluble fraction are available in the literature, the global variability of the CF is reduced to 1.76 orders of magnitude (Plouffe et al., 2015, 2016). In a similar study using linear regression models instead of WHAM to assess the Cu and Ni speciation in soil to determine their terrestrial ecotoxicity, Owsianiak et al. (2013) highlighted a global CF spatial variability of 3.5 for Cu and 3 for Ni (Owsianiak et al., 2013).

After the Clearwater consensus (Diamond et al., 2010) it was recommended not only to include metal speciation in terms FF and of BF (bioavailability factor), but also to be consistent when calculating the effect concentrations (Diamond et al., 2010). The Free Ion Activity Model (FIAM) and Biotic Ligand Model (BLM) allow predicting the effect concentration of a metal in aquatic environment accounting for its speciation. BLM uses a mechanistic approach that is based on the hypothesis that the metal–biotic ligand interaction can be represented like any other chemical reaction of a metal species with an

organic/inorganic ligand. The toxicity of metals to organisms is assumed to occur as the free metal ion is reacting with the organisms' binding sites (Di Toro et al., 2001; Niyogi & Wood, 2004). This model calculates the complexation with the biotic ligand using the metal stability constants (LogK_{Me}) and the dissolved organic carbon content of water (DOC) and it also considers competition with other cations present in the water (Ca^{2+} , Mg^{2+} , K^{+} , H^{+}). Currently, acute and chronic BLM are available for Cu (Daphnia, Fish), Ni (Algae, Daphnia, fish), Zn (Daphnia, fish and algae), Cd, Pb and Ag. Gandhi et al. applied BLM to calculate effect factors (EF) for Cu, Ni and Zn and showed that speciation of metals in aquatic environment lowers the toxicity by 5-50 times (Cu, Ni, Zn) depending on metal and selected water chemistry (Gandhi et al., 2010).

From all these studies, it is evident that metal speciation plays a critical role in metal fate and impact in natural aquatic and terrestrial ecosystems and that the consideration of total metal concentration should be avoided in fate and characterization calculations. All those existing studies highlight that there is an evident need to consider the metal speciation both in soil and in water in ecotoxicity impact assessment. Hence, the calculations of metal soil and water toxicity should be based on regional properties for soil, subsoil and freshwater.

In the current version of USEtox, the sub-soil compartment is considered as a sink for the substances: the fraction of contaminant that reaches the groundwater compartment through its fate “disappears” and is never transferred to the surface water. This may be an appropriate assumption for most organic chemicals, which may degrade before the resurgence of groundwater as the groundwater flow is slow, but this assumption may represent an important bias for the metals, which are not biodegradable and may travel from soil to groundwater through the deeper soil layers, and ultimately to freshwater. The metal fate may therefore not be properly addressed within USEtox.

Most of the aquifers and groundwater tables are interconnected with the freshwater bodies and changes in their quality or quantity affects freshwater (Fleckenstein, Krause, Hannah, & Boano, 2010). Water movement between groundwater and surface water is a major pathway for chemical transfer between terrestrial and aquatic systems (de Souza Machado, Spencer, Kloas, Toffolon, & Zarfl, 2016; Menció & Mas-Pla, 2008; Winter, 1998). By not considering the fate of metal through groundwater, the fate of metals to the soil is overestimated (which appears as the ultimate compartment where most of the metal emitted to soil “disappears” from the system when

transferred to groundwater) and the fate of metal to the surface water is underestimated (as metals reaching the groundwater never potentially reaches surface water in the model).

After precipitations, a fraction of the rainwater infiltrates through the land surface and moves vertically downward to the water table. The ground water then moves slowly both vertically and laterally with a three-dimensional flow, which moves along flow paths of varying lengths from areas of recharge to areas of discharge. A watershed (analogous with 'drainage basin' or 'catchment area') is defined as an area of land that drains down the precipitation until it reaches the same water body (a river, a lake or the ocean). Watershed boundaries are based on soil topography, watercourse and stream locations. The watershed can be considered as the geographical resolution level at which any raindrop that falls on the soil will reach the same water body (and so do all the contaminants transported by this water flow if not degraded before).

Estimation of the groundwater behaviour requires modelling of the interaction between all of the important processes in the hydrologic cycle, such as land cover, soil profile, infiltration, surface runoff, evapotranspiration, snowmelt and variations in groundwater. The quantitative description of the hydrologic processes may become very complicated due to the high uncertainty and complexity in the underlying physical parameters (Jyrkama & Sykes, 2007). However, in LCIA, toxic impact assessment is generally conducted using simplified steady-state models such as USEtox. One of the important principles of USEtox is to be parsimonious and to include only the most relevant environmental mechanisms. Hence, the integration of the transfer of contaminant through groundwater in LCIA should also be done parsimoniously in an adapted version of USEtox, only allowing to quantify the mass of contaminant transferred from soil to surface water at steady state through groundwater, without details about the pathway of the contaminant in the subsoil / groundwater compartment and about the hydrologic processes kinetics.

The objective of the present study is to develop such a version of USEtox to calculate regionalized freshwater ecotoxicity characterization factors (CF) for metal soil emissions accounting for the missing link from topsoil to freshwater through groundwater and considering speciation in all the environmental compartments (soil, subsoil & groundwater, freshwater) and to apply it to the case of Zinc as a proof of concept.

Zn was chosen because despite of being a trace metal in earth's crust it can lead to toxic effects when it is found in the environment in excess. At lower pH, free Zn is very soluble and mobile divalent trace

cations and therefore often one of the most phytotoxic trace element after free Al and Mn. Zn is used in industries as protective coating against corrosion, as a catalyst in various chemical processes (eg rubber, pigments, plastics, lubricants and pesticides), in batteries, automotive equipment, etc. (Kabata-Pendias, 2010). Thus, it is important to better evaluate its ecotoxicological impacts. Zn is also a major contributor to the average Canadian's ecological footprint primarily in relation to terrestrial ecotoxicity (Lautier et al., 2010). In addition, according to Pizzol et al. (2011a) the contribution of Zn to ecotoxicity is highly variable according to the chosen LCA methods (Pizzol et al., 2011a; Plouffe, 2015). Further study on Zn therefore becomes crucial in determining its actual contribution.

4.4 Methodology

Figure 4-1 summarises all the methodological steps that are detailed in the next subsections. In summary, 1) the first step is to determine the soil/water partitioning coefficients (K_d) for Zn in soil and in subsoil using the WHAM7 speciation software for all the different soil and subsoil units from the harmonized world soil database (HWSD v.1.2) – as already done for the topsoil by Plouffe et al. (2015, 2016) making the assumption that the entire soluble Zn fraction is mobile and travels with water through the soil column and reaches the groundwater and, ultimately, the surface water. 2) Once the metal reaches freshwater, the labile (true solution) fraction of Zn in freshwater is calculated using WHAM 7 as being the bioavailable fraction for freshwater ecosystems, as recommended by the Clearwater consensus (and as already operationalized by Dong et al. (2014); Gandhi et al. (2010) using the freshwater properties in the different watersheds (basins and sub-basins) around the world, using the water properties available from different databases GEMStat, EuroGeoSurveys, etc. (GEMStatPortal (2017)). This true solution fraction is used to determine watershed specific suspended solid – water partitioning coefficient (K_{pss}), organic carbon – water partitioning coefficients (K_{DOC}), bioavailability factors (BF) and effect factors (EF) – those last being determined using BLM. 3) The third step is to intersect the watersheds (basins and sub-basins) with the soil units from the HWSD database using geographical information system (GIS) to generate the native resolution geographical cells that will have the soil and subsoil K_d s from the soil unit (determined at the first step) and the freshwater K_{pss} , K_{DOC} , BF and EF from the receiving watershed. 4) A modified version of USEtox is created in which the groundwater compartment is connected to the soil and to the surface water compartments. For each native resolution cell, the

fate and characterization factor of Zn is calculated by considering that Zn has different properties in each cell (ie the soil and subsoil specific K_{ds} in soil and groundwater compartment respectively and the receiving watershed specific K_{pss} , K_{DOC} , BF and EF). 5) The results obtained at the native resolution scale are aggregated at different more operational regionalization scales: watershed, country, continent and global level. The corresponding spatial variability due to aggregation at a coarser scale is determined 6) The results are compared to the default values of USETox.

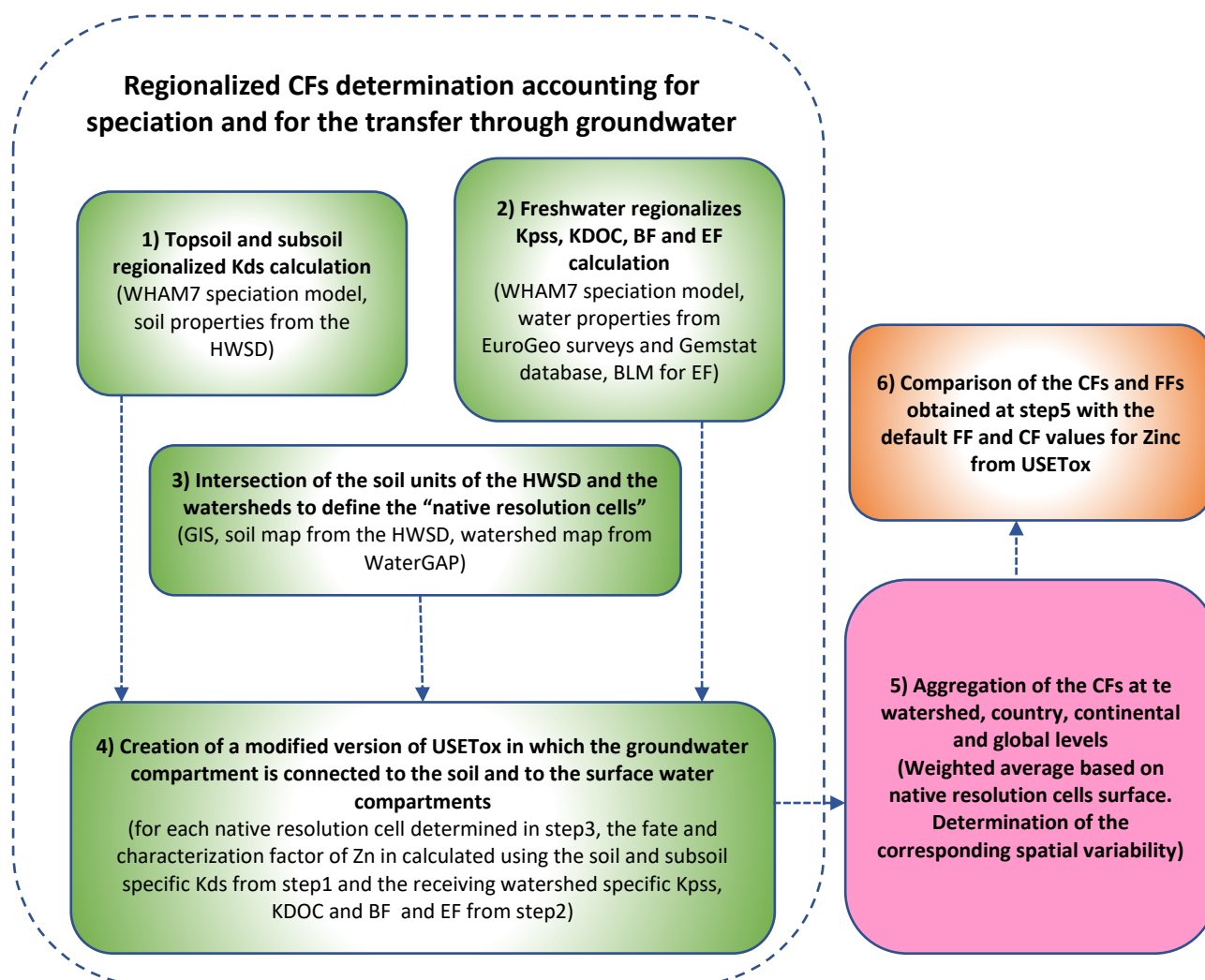


Figure 4-1 General methodological steps followed for this study

4.4.1 Topsoil and subsoil regionalized partitioning coefficients calculation

We used the speciation model WHAM7 (Lofts, 2012) to calculate metal speciation in soils since it is the most recent version of the WHAM model, which was recommended for metal speciation assessment in LCIA in the Clearwater Consensus (Diamond et al., 2010) and since various researchers have already used the WHAM model in LCIA to determine metal speciation both in soil and in water (Diamond et al., 2010; Gandhi et al., 2010; Plouffe et al., 2015). Moreover, the validity of the WHAM model to predict Zn soluble fraction in soil using only the soil properties

available in the HWSD (ie pH, CEC, DOC, Na⁺, Ca²⁺, Mg²⁺, K⁺, SO₄²⁻, Cl⁻) was validated by Plouffe et al. (2016).

The speciation calculations were done following the methodology from Plouffe et al. (2016) considering the major soil attributes available in the HWSD v1.2 database (pH, CEC, DOC, Na⁺, Ca²⁺, Mg²⁺, K⁺, SO₄²⁻, Cl⁻) and assuming the background Zn concentration following the guidelines from Kabata-Pendias (2010) as per soil texture. This was done for all the available soils (16166 soil units) and subsoil units (13700 soil units) from the HSWD.

We are making the assumption that the transportation of Zn in soil and in the aquifer occurs only in the aqueous phase and that all the soluble Zn species are mobile with water in the soil and the subsoil. Hence, our calculated K_{ds} for soils and sub-soils are based on the soluble fraction of Zn ([Zn]_{soluble}) (see Equation 17).

$$K_d = \frac{[Zn]_{soluble}}{[Zn]_{soil}}$$

Equation 17

The soluble fraction comprises free ion, true solution complexes and species bounded to colloidal phases (Lofts, 2012), all the remaining Zn species being considered as the fraction of Zn in soil ([Zn]_{soil}). We consider that this soluble fraction is moving along with the leached flow from soil to subsoil and from subsoil to surface water, hence, the simplifying assumption is that the speciation in groundwater is the same as in the subsoil. We are aware this is a far from perfect proxy, but the groundwater properties around the world are too poorly documented to have a better assumption.

4.4.2 Freshwater regionalized partitioning coefficients, bioavailability factor and effect factor calculation

4.4.2.1 Watershed map choice

Depending on the publications, the watershed geographical limits may vary slightly. In regionalized LCIA, some watershed maps are already used for other impact categories than toxicity/ecotoxicity (Freshwater eutrophication, water use impacts) (A. M. Boulay, Bouchard, Bulle, Deschenes, & Margni, 2011; Helmes, Huijbregts, Henderson, & Jolliet, 2012). The AWARE consensual model for water scarcity impact assessment in LCA uses the watershed definition from the WaterGap project (A. M. Boulay et al., 2011; Döll, Kaspar, & Lehner, 2003). For coherence purpose across impact categories in LCIA, we decided to adopt the same map.

4.4.2.2 Calculation of the regionalized partitioning coefficients and bioavailability factor in water

Consistently with what was done in soils and sub-soils, we used the speciation model WHAM7 to determine the speciation in freshwater. The speciation calculation were done following the methodology from Gandhi et al. (2010) considering the major water properties (pH, DOC, alkalinity/hardness/ CaCO_3 , Na^+ , Mg^{2+} , Al^{3+} , Ca^{2+} , K^+ , SO_4^{2-} , Cl^-). The needed properties to apply this methodology are not available in a single global database. Hence, data were collected from different sources covering different regions of the world with a different level of completeness and geographical resolution For Europe, the Forum of European Geological Surveys (FOREGS, now EuroGeoSurveys) database (BGS_NERC, 2017) was used. For Canada, the Canadian aquatic data based on the Ecozones are collected from Wiken (1996) and Gandhi, Huijbregts et al. (2011) were used. For the other regions of the world, we used available data from the GEMStat portal (GEMStatPortal 2017) database, which allowed covering the regions of Central & South America, Russian federation and some parts of Africa. Some data gaps were also completed by extrapolating some data using the neighbouring watershed data (see details in supporting information section 1).

When available, the listed dissolved Zn concentrations from the databases and from the literature are used for Zn speciation calculation. In some cases, dissolved Zn concentration was not available and a background value of $2\mu\text{g/L}$ was assumed. This value is an average estimation of the dissolved

Zn found worldwide in sites where no anthropogenic contaminations were detected (ATSDR, 2005; BGS_NERC, 2017; CCME, 2016; GEMStatPortal, 2017; Shiller & Boyle, 1985). This value seems an appropriate proxy given that a) the average dissolved background Zn concentration in European water is 2.65 µg/L (calculated from the data available in the FOREGS database); b) according to US agency for toxic substances and disease registry (ATSDR, 2005), the average dissolved background Zn concentration in major US rivers is 1.9 µg/L (ATSDR, 2005) ; c) in some water bodies in Quebec (Canada), the dissolved Zn concentration in pristine environment is reported to be around 1 µg/L (CCME, 2016); d) In Norwegian, Swedish and Finnish lakes, background Zn concentrations are found to be respectively 1.54, 1.27 and 1.80 µg/L. In some cases for groundwater, the dissolved Zn concentration is found up to 10 µg/L and up to 4.1 µg/L for freshwaters in Sweden and surface water dissolved Zn ranged from 1.0 to 2.2 µg/L in northern and southern Sweden (Landner & Reuther, 2005). Although, Zn concentration and Zn solubility are highly dependent on temperature, pH and DOC, this is a fair assumption since data are limited and our assumed value is also under the maximum permissible limit (MPA) for dissolved Zn in freshwater set by RIVM for European water (3µg/L to 7.8µg/L for lowland waters) (Bodar, 2007). The ratio between suspended particulate matter (SPM)-bound/particulate ([Zn]_{particulate}) and truly dissolved metal concentration is expressed as K_{pss} (unit L/kg). Similarly, K_{DOC} (unit L/kg) represents the ratio between dissolved organic carbon (DOC)-bound/ colloidal ([Zn]_{colloidal}) and truly dissolved metal concentration (Equation 18& Equation 19).

$$K_{pss} = \frac{[Zn]_{particulate}}{[Zn]_{true\ solution}}$$

Equation 18

$$K_{DOC} = \frac{[Zn]_{colloidal}}{[Zn]_{true\ solution}}$$

Equation 19

Bioavailability factors (BF) were calculated based on the recommended methodology in the Clearwater workshop (Diamond, Gandhi et al. 2010) and the method followed by Gandhi, Diamond et al. (2010) as ratio of the true solution Zn to total Zn concentration. The true solution concentrations were calculated from WHAM7 results ([Zn]_{true solution}) and comprises the free ion and the true solution complexes (Equation 20).

$$BF = \frac{[Zn]_{True\ solution}}{[Zn]_{total}}$$

Equation 20

4.4.2.3 Calculation of the Effect Factors

Following the methodology from Gandhi, Diamond et al. (2010), we have used the BLM (Di Toro et al., 2001) model to calculate Zn Effect Factors (EF, in PAF-m³/Kg), considering the free metal ion concentration as being the one contribution to the toxicity to be consistent with the calculation of BF based on true solution, for all the watersheds for which the data needed to determine the speciation was found. BLM parameters are available for Daphnia. For fish and algae we have extrapolated the BLM parameters (Conditional stability constants-LogKs) from Cheng and Allen (2006), assuming that LogKs for cations and the biotic ligand, mechanism of binding, and modes of action are similar across the organism class, as already done previously by Gandhi et al (2010). The resulting BLM models for daphnia, fish and algae were used to determine watershed specific EC50 for each of the three species. These EC50s were then used to calculate the EF using Equation 21.

$$EF = \frac{0.5}{HC50_{EC50}}$$

Equation 21

4.4.2.4 Intersection of the soil units of the HWSD and of the watersheds to define the “native resolution cells”

The native resolution cells are obtained by intersecting the HWSD soil map and the WaterGAP watershed map using QGIS (Quantum GIS 2.18).

The HWSD-database (2014) soil database is composed of a GIS raster image file which links to a soil attribute database all over the world. The underlying map is in 30-arc-second grid-cells, corresponding to 16112 soil mapping units (SMU or MU_Global) which then are converted as vector layer for in QGIS for calculation.

The World drainage basins or watersheds map from WaterGAP (Courtesy of: Döll et al. (2003)) was generated from world's 34 biggest river basins (downstream) and later subdivided into >11000 smaller sub-watersheds. We have intersected the soil map with the sub-watershed level map, however, for some instance the information on parent watersheds (which comprises with more than one sub-watershed) was taken from UN-Global (2016) database. These watersheds are paired with the aquatic properties data described in section 4.4.2.2 for the different watersheds of the world for which this data was available. Some regions being better documented than other about the water properties, the properties are sometimes available at the sub-watershed level, when in other regions, only a few samples are available in a whole watershed. When data was available at the sub-watershed level, it was preferred. When no data was available at the sub-watershed level, the median value for the watershed was used. The variability of the documented properties across the samples available in the watershed or the sub-watershed was averaged since the observed data were spread for different seasons over few years and it no consistent specific orders or numbers of measurements were maintained (GEMStatPortal, 2017). The native resolution scale cells resulting from the intersection of this soil map and this watershed map are considered to have the soil properties from the soil map and the water properties from the (sub)watershed.

4.4.2.5 Creation of a modified version of USEtox in which the groundwater compartment is connected to the soil and to the surface water compartments

In USEtox, the instantaneous equilibrium assumes intermittent rain being the primary carrier of chemical deposition from air onto soil, then runoff event carrying the deposited chemicals from the soil surface to the surface water and a fraction of rain that is leaching the chemicals from topsoil. According to the model structure, half of net precipitation onto soils is evaporated, with the remaining half being split equally between surface water runoff (25%) and water infiltration (25%) through soil (See Equation 22; representation of transfer from soil to water in k-matrix) (Henderson, Hauschild et al. 2011).

$$Transfer\ soilToWater(USETox) = \frac{\frac{rainrate * runoff\ fraction}{dimensionless\ soil - water\ part.\ coeff} + Erosion}{Depth_{soil}}$$

Equation 22

While considering this fraction of runoff from soil to water is reasonable, since it is being received by another compartment, by contrast, another 25% of the rain which is the fraction infiltrating (leaching) via soil is considered lost from the system (See Equation 23: how current USETox calculated removal rate of chemical from soil compartments). This fraction has not been accounted as reaching any other compartments.

Removal from soil Comp. (USETox)

$$= \frac{rainrate * fraction\ infiltrating\ through\ soil}{dimensionless\ soil - water\ part.\ coeff * Depth_{soil}}$$

Equation 23

To remedy this, we propose to connect the ‘lost’ portion of metal contained in the fraction infiltrating through soil with the freshwater compartment (Figure 4-2).

We have modified USETox

- by adding this contaminant removal from soil compartment within the subsoil/groundwater compartment.
- by defining these groundwater compartments as having the same surface area as the soil compartment in USETox at the continental and global scale with a depth of 100cm, which is also the reported depth of subsoil in the HWSD database (HWSD-database, 2014). Total volume of groundwater at the global scale of $10.7E+15\ m^3$ collected from Margat (2008).
- The porosity of the Subsoil & Groundwater compartment is 48% which is calculated from soil particle density and average bulk density in HWSD database (See supporting info).

- With the consideration of the inclusion of the groundwater compartment, the transfer coefficient (K_d -subsoil) is added within the calculation which is calculated using the methodology described in section 3.1),
- By considering that the soluble fraction of contaminant in the groundwater compartment is going to be transferred to the continental water compartment (freshwater) in order to establish the link between soil and freshwater (Equation 24).

Transfer from soil to water Comp. (modified USETox)

$$= \frac{\text{rainrate} * \text{fraction infiltrating through soil}}{\text{dimensionless soil} - \text{water part. coeff} * \text{Depth}_{\text{soil}}} + \frac{(\text{removal from soil comp. via leaching} * \text{vol. of water in groundwater comp.})}{\text{vol. of water in groundwater comp.} + (K_d \text{ subsoil} * \text{volume of soil in groundwater comp.})}$$

Equation 24

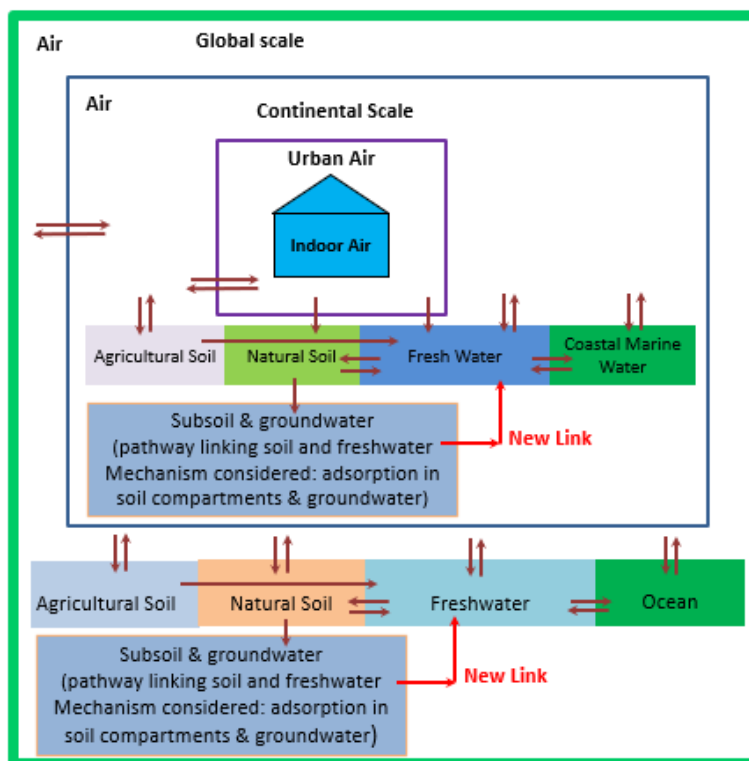


Figure 4-2 Modification of the fate model in USETox

The removal matrix (k-matrix) is modified which is made up of all the removal rates from different compartments and this process will eventually change the output in fate matrix (the fate matrix in USETox is the inversion of the k-matrix) (Rosenbaum et al., 2007). This way the law of mass conservation is not violated as this is simply addition of a mass fraction to another recipient with the consideration that part of the metal is being sorbed onto the soil surface and part of it are getting carried along with the water flow into the freshwater system.

The removal rates in k- matrix are calculated based on the pollutants' standard chemistry included in USETox's substance database. These removal rates are calculated based, among other environmental mechanisms, on the substance's partitioning coefficients in soil, sub-soil and water, the effect factor and the bioavailability factor in water. For each native resolution scale cells, the

properties influenced by speciation and calculated in steps 1 and 2 are used (K_d in the soil and subsoil cells, K_{pss} , K_{DOC} , BF, EF).

4.4.2.6 Aggregation of the CFs at the watershed, country, continental and global levels

CFs at the native resolution scale are hardly operational in LCA context, hence there is a need to calculate aggregated CFs at broader geographical scales with the corresponding uncertainty. As the probability of Zn emission to soil in the different native resolution scale cells is unknown, we considered as a proxy that this probability is proportional to the cell surface. In our calculation, it was assumed that each contributing soil cells are equally important and any emission in soil is uniformly distributed over the entire soil or watershed unit before passing to the next compartment. Hence, the characterization factor at the watershed level, the country level, the continental scale and the global scale CF_{agg} is equal to the weighted average of all the native resolution scale cells i $CF_{native, i}$ contained in the watershed, the country, the continent and the world using the cells surfaces S_i as weighting factor (Equation 25).

$$CF_{agg} = \frac{\sum_i S_i * CF_{native, i}}{\sum_i S_i}$$

Equation 25

For each CF_{agg} , the spatial variability within the broader geographical cell is documented using with their minimum, maximum, average, median value, frequency of occurrence and percentiles.

4.4.2.7 Comparison of the CFs obtained at step 5 with the default CF values for Zn from USEtox

The CF_{sw} values obtained at the different geographical scales are compared with the USEtox generic value of soil to water CF_{sw} for Zn emitted to soil in order to see the influence of the modifications done to the model and to determine if the speciation and the transfer through groundwater are environmental mechanisms influent enough to be worth being integrated in USEtox.

4.4.3 Results and discussions

4.4.3.1 Topsoil and subsoil regionalized K_d s

The obtained K_d s for each soil cell of the HWSD can be found in supporting information section for topsoil and subsoil. Topsoil K_d s range from $5.58E+01$ L/Kg to $9.29E+16$ L/Kg, varying over 15 orders of magnitude with a median of $3.12E+04$ L/Kg. Subsoil K_d s also showed a wide variability (16 orders of magnitude) from $4.64E+01$ to $1.05E+17$ L/Kg with a median of $1.66E+04$ L/kg. Both the topsoil and subsoil medians are far from their average values which points out to their outliers on both ends (topsoil average $K_d=1.36E+13$ L/Kg ; subsoil $K_d= 1.59E+13$ L/Kg) signifying wide variability in world soil characteristics. The lower K_d values were found for soils with high organic matter content with a moderate clay and quartz concentration. However, few extreme K_d values (on higher side) in Africa (larger than $1E+07$), were possibly due to the sandy soils in some specific soil units and therefore in watersheds (Orange and Vaal river watersheds) where contributing soils have more than 60% sand (Arenosols, Leptosols and Cambisols), which exhibit high quartz content with very poor organic matter content, and higher pH value (≈ 8.3) which led to higher partition coefficients (S. Hassan, Garrison, Allen, Di Toro, & Ankley, 1996; HWSD-database, 2014). However, 90% of the K_d values are between $1.01E+03$ L/kg and $9.7E+6$ L/Kg (5th and the 95th percentile) which means we can accept the median value of K_d for topsoil and subsoil. 88% of the total number of soils for topsoil and 98% for the subsoil K_d values occur between 3rd and 4th order of magnitude (Figure 4-3). However, caution should be taken if using the generic value of K_d since it might be far enough to represent the world or that specific soil or watershed.

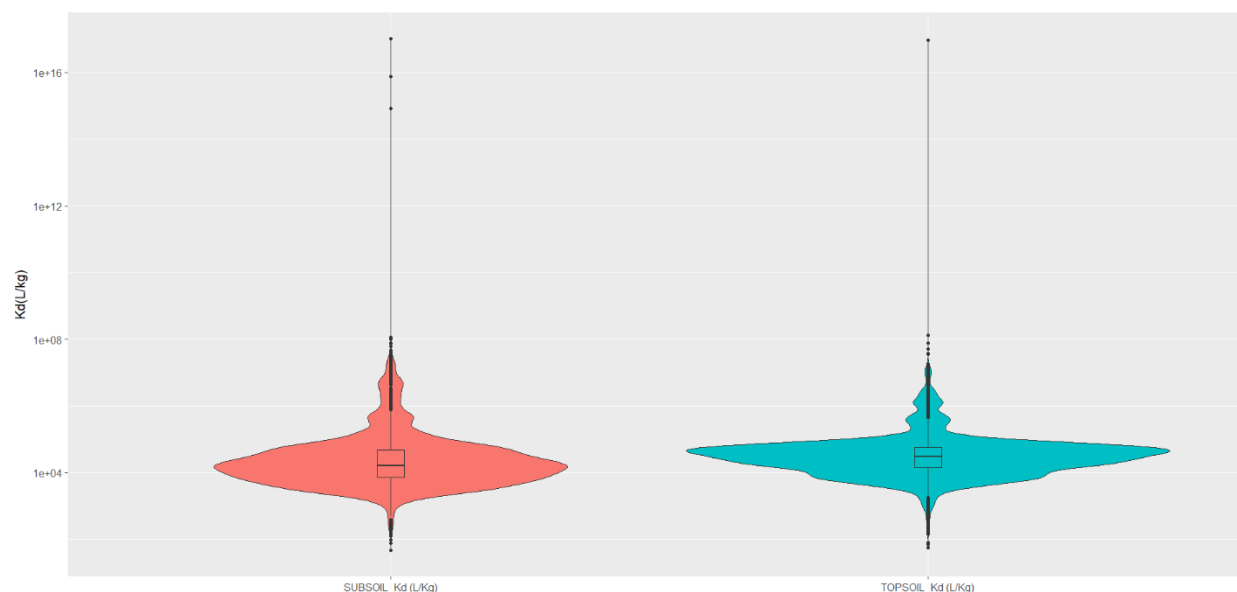


Figure 4-3 Violin plot showing the variability of the soil-water partitioning coefficient in top soils (K_d), subsoil & groundwater (K_d) compartments. The violin representing the probability density and the box plots representing the, values with 95% confidence interval, median values and the interquartile ranges.

4.4.3.2 Freshwater regionalized K_{pss} , K_{DOC} , BF and EF

The obtained K_{pss} , K_{DOC} , BF and EF for each watershed can be found in supporting information file (ESM-2).

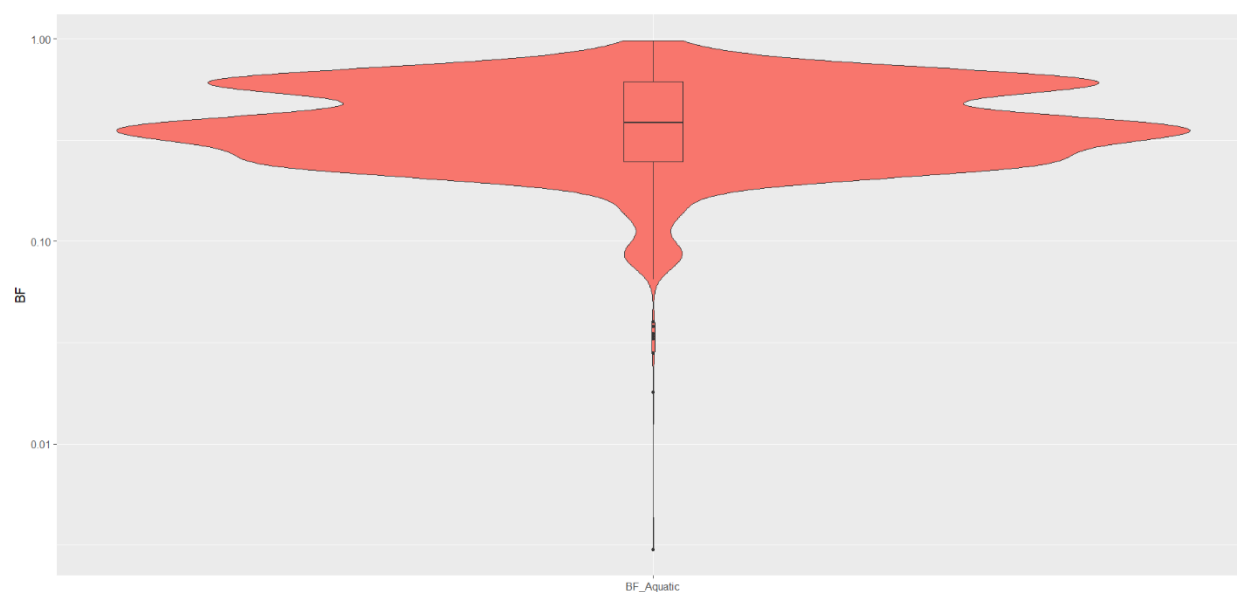
The regionalized freshwater K_{pss} at the watershed scale varied over 7 orders of magnitude across the globe (1.96 to $2.05E+07$ L/Kg), with a median value of $1.34E+04$ L/Kg. The regionalized freshwater K_{DOC} values ranged from $1.02E+01$ L/Kg to $2.37E+06$ showing a variability of 5 orders of magnitude all over the world. Given that, the K_{pss} and K_{DOC} found in Gandhi et al. (2010) and Dong et al. (2014) for Zn varied over 1-2 orders of magnitude over Europe, however, our values were calculated from all aquatic data around the globe, so the variation in their results are to be expected.

The regionalized BF varied over 2 orders of magnitude across the globe ($3.10E-3$ to $9.82E-1$), with a median value of $3.85E-01$ and an average value of $4.07E-01$ (Figure 4-4 a). Compared with the

values found in Gandhi et al. (2010) ($1.32\text{E-}1$ to $9.79\text{E-}2$) and Dong, Gandhi et al. (2014) ($1.9\text{E-}1$ to $7.4\text{E-}1$), less variations are expected since their studies were limited for Europe. Our median and average values of BF are in the same order of magnitude for the entire world, however, it is not because there are little variations in worlds' water properties rather lack of aquatic data available.

The regionalized EF varied over 3 orders of magnitude across the globe ($8.35\text{E+}01$ PAF.m³/kg to $9.75\text{E+}04$ PAF.m³/kg), with a median value of $4.69\text{E+}03$ PAF.m³/kg and an average value of $5.79\text{E+}03$ PAF.m³/kg (Figure 4-4 b). Our calculated value is little higher but in the same order of magnitude with the USETox generic EF value ($2.84\text{E+}03$ PAF.m³/kg). Average ecotoxicity (HC50EC50) for Zn is $2.46\text{E-}04$ kg/m³. For Europe, our effect factor varied over 1 order of magnitude ($1.85\text{E+}02$ PAF.m³/kg to $9.82\text{E+}03$ PAF.m³/kg) as also found by Gandhi et al. (2010) and Dong et al. (2014) with a median value of $2.41\text{E+}03$ PAF.m³/kg.

(a)



(b)

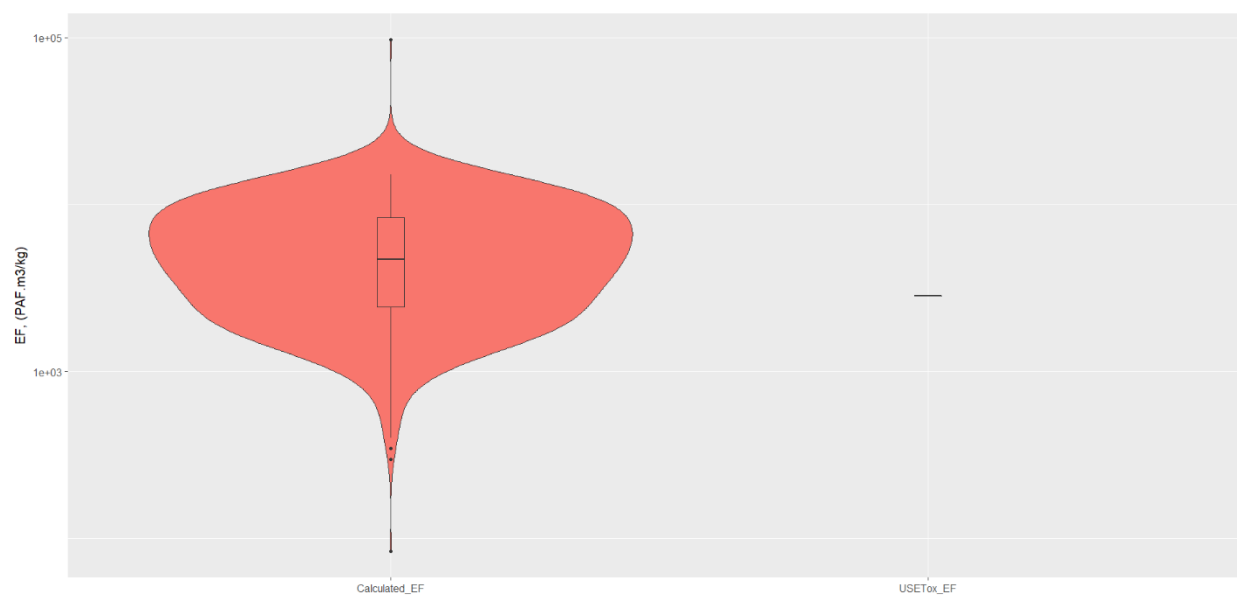


Figure 4-4 Plots showing the variability and distribution in a) Bioavailability factors (BF) and b) Effect factors (EF) for all water properties around the world

4.4.3.3 Intersection of the soil units of the HWSD and of the watersheds to define the “native resolution cells”

The correspondence between the native resolution (sub-watershed) and the HWSD soil units resulting from the overlap of the HWSD soil units and the watershed maps is available in supporting information in excel format (ESM-3).

This overlapping of the two maps resulted in 5327 native resolution cells for which both topsoil and subsoil units are found to perform necessary calculations.

4.4.3.4 Results from modified version of USEtox in which the groundwater compartment is connected to the soil and to the surface water compartments

The FF and the CF obtained at the native resolution scale are also available in the supporting information section (ESM1 and ESM2), which documents the results of the modified version of USEtox for all the native resolution scale cells. Figure 4-5 a and Figure 4-5 b shows respectively the distribution of the native resolution scale FF and CF at the continental and at the global scales. Spatial variability in FF_{sw} (min-max values) for Africa, Asia, Australia, Canada, Europe, Mexico & central America, Russia, South America and USA are: 2.85E+01 to 4.27E+01 days for Africa, 5.25E+01 to 7.88E+01 days for Asia, 1.88E+01 to 2.81E+01 days for Australia, 1.14E+01 to 1.33E+02 days for Canada, 3.06E+02 to 4.57E+05 days for Europe, 2.61E+01 to 3.91E+01 days for Mexico & Central Americas, 8.68 to 2.93E+01 days for Russian Federation, 1.52E+01 to 7.83E+01 days for South America and 8.21 to 1.28E+02 days for USA.

The spatial variability in FF_{sw} around the world ranged over two orders of magnitude (8.55 to 1.27E+02 days) with a median value of 4.23E+01 days. The generic USETox value for FF_{sw} is 4.78E+01 days, which is amazingly close to our global median calculated by default USETox. Although all the regions showed larger spatial variability in native resolution (watershed) K_d s, which were calculated from topsoil and subsoil K_d s (see 4.4.2.4 for more information on how it was calculated) within that area of that specific watershed (see 4.4.3.1 and Figure 4-5 a) (5 orders of magnitude for Australia, Canada, USA, 6 orders of magnitude for Mexico & C.America and Russia, 7 orders of magnitude for Asia, Europe and S.America and 16 orders of magnitude for Africa), the soil-to-water metal fate factors (FF_{sw}) showed a variability of 2 orders of magnitude which is within USETox's acceptable uncertainty range for results (Sébastien Humbert, Schryver,

Bengoa, Margni, & Jolliet, 2014). Interestingly, 80% of the total number of calculated native resolution FFsw varied within the same order to magnitude ($1.71\text{E}+01$ to $8.2\text{E}+01$ days) which means a single value from this range can represent global soil to water fate factor.

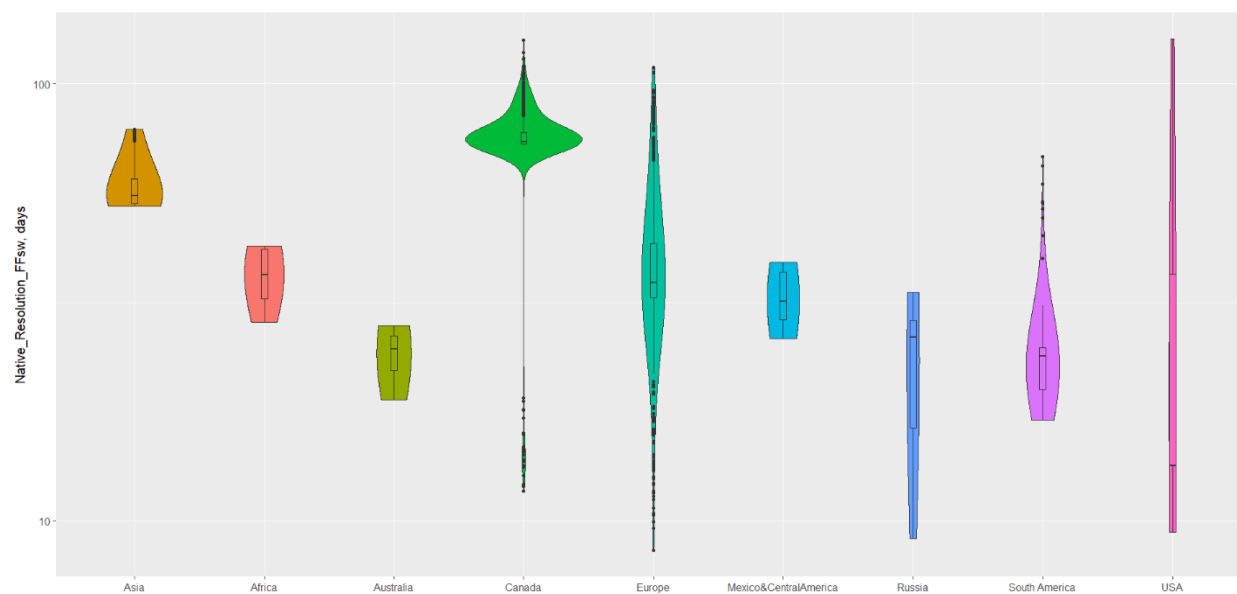
The calculated native resolution scale soil to water characterization factors (CFsw) varied over 3 orders of magnitude ($2.44\text{E}+02$ to $3.50\text{E}+05$ PAF.day.m³/kg) at the global scale. Figure 4-5 b shows the frequency and distribution of the average world CFsw with the most probable value for (sub) watershed CFsw being $9.55\text{E}+04$ PAF.day.m³/kg. The USETox default CFsw for soil to water is slightly higher than our calculated value ($1.36\text{E}+05$ PAF.day.m³/kg), but again, falls within the acceptable uncertainty range in LCA (Sébastien Humbert et al., 2014).

When we compare the continent/region specific CFsw as per our calculation method, we find greater spatial variabilities are observed in regions where freshwater properties data were available (Europe, Canada, South America). As discussed in the previous section for FFsw results, despite having 7 orders of magnitude of spatial variability of the soil K_d in Asia, Europe and South America, only Europe (with UK) showed a greater spatial variability in CFsw of 3 orders of magnitude ($3.06\text{E}+02$ to $4.45\text{E}+05$ PAF.day.m³/kg), with the median value being $4.10\text{E}+04$ PAF.day.m³/kg (Figure 4-6).

For Canada, freshwater properties data were aggregated over the ecoregions. The CF results showed a spatial variability of almost 2 orders of magnitude ($3.69\text{E}+03$ to $1.18\text{E}+05$ PAF.day.m³/kg) within the country from one ecozone to another. For south America, for characterization calculation, water properties located on smaller sub-watersheds were aggregated over bigger watershed like the Amazon river and the Parana river watersheds. These two watersheds are the biggest watersheds in South America and covers almost 50% of the entire continent. For Amazon river watershed CFsw s varied over 2 orders of magnitude ($2.16\text{E}+4$ to $2.84\text{E}+05$ PAF.day.m³/kg) whereas for Parana river watershed the range of CFsw was on same order or magnitude ($1.39\text{E}+04$ to $7.16\text{E}+04$ PAF.day.m³/kg). The CFsw for the entire continent stayed within the range of these two large watersheds CF values ($1.39\text{E}+04$ to $2.84\text{E}+05$ PAF.day.m³/kg). For Russian Federation, aquatic properties were available for few major watersheds (data collected from the GEMStatPortal (2017) database) and the average values from these properties were aggregated for the rest of the watersheds all for the country. CFsw s ranged over 1 orders of magnitude ($1.41\text{E}+03$ to $1.66\text{E}+04$ PAF.day.m³/kg). For Africa, Asia and, CFsw

s ranged from $3.77\text{E}+04$ to $7.86\text{E}+04$ PAF.day.m³/kg, $2.21\text{E}+05$ to $3.32\text{E}+05$ PAF.day.m³/kg and $1.4\text{E}+04$ to $2.09\text{E}+04$ PAF.day.m³/kg respectively. For Australia, CFsw stayed over the same order of magnitude.

(a)



(b)

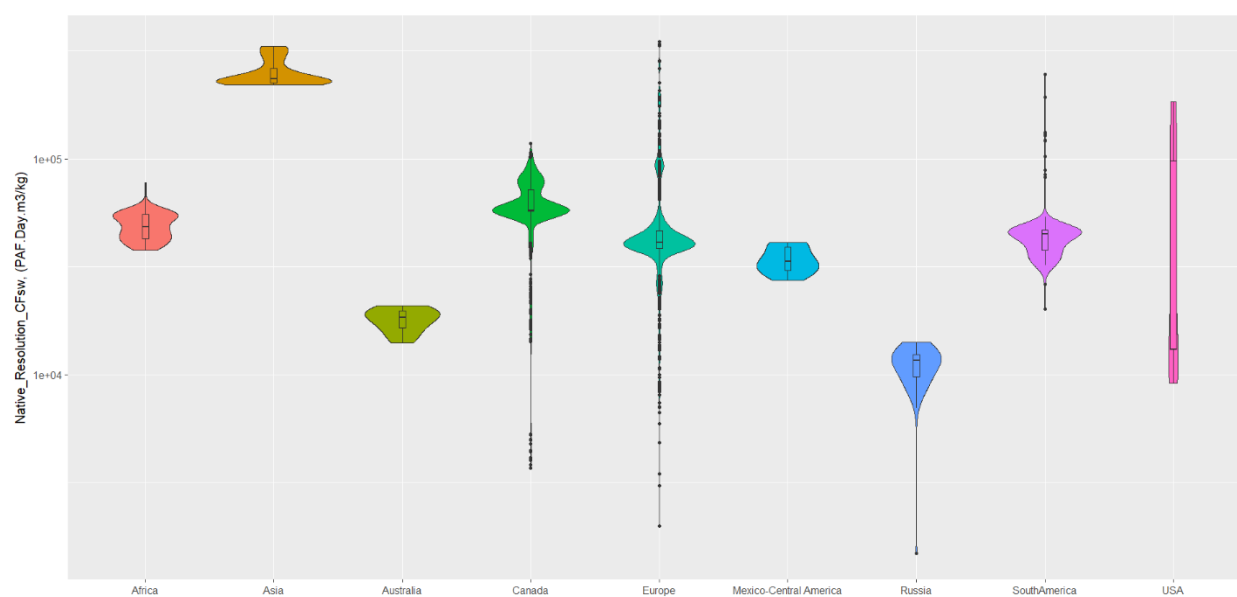


Figure 4-5 Variabilities at the native resolution scale regionalized values of (a) the soil to water fate factors (FFsws) and (b) the freshwater ecotoxicity characterization factors (CFsw) for an emission to soil

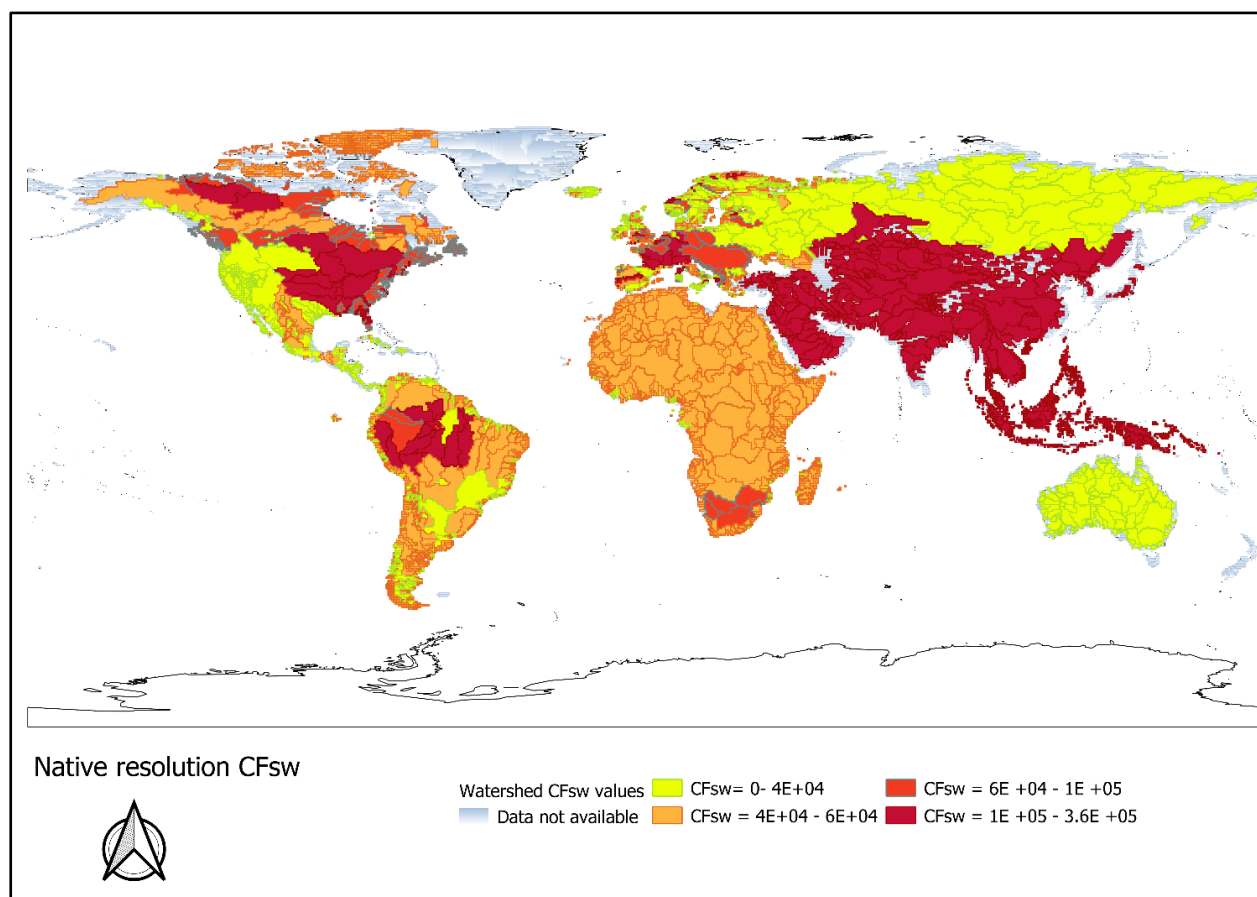


Figure 4-6 Soil to water characterization factors (CFsw) for watersheds for different regions of the world

4.4.3.5 Aggregation of the CFs at the watershed, country, continental and global levels

The values of the aggregated CFsw s at the watershed and regional (country/ continental/ global) levels with their corresponding spatial variabilities are available in supporting information (EMS-1 and ESM-2).

USEtox calculated value for soil to water characterization factor is $1.36\text{E}+05 \text{ PAF.day.m}^3/\text{kg}$ which is close to our calculated aggregated CFsw value ($9.18\text{E}+04 \text{ PAF.day.m}^3/\text{kg}$) for the world after the inclusion of groundwater compartment and metal speciation (Figure 4-7).

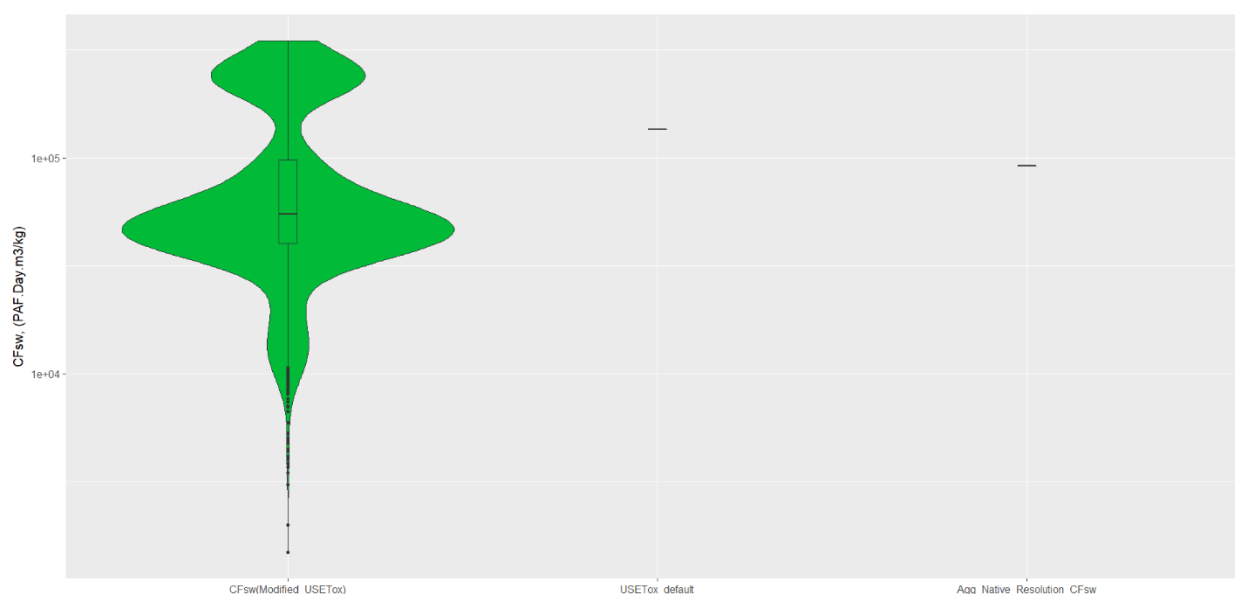


Figure 4-7 Spread and frequency of the soil to water characterization factors (CFsw) with the aggregated CFsw value and the default USEtox value

4.5 Conclusions

This work is an important step in regionalized assessment of metals in LCIA with the inclusion of watersheds. We observed a large spatial variability the soil and water properties across the different soils and watersheds of the world. However, apart from certain outliers (in particular sandy soils in Africa), most soils show a reasonable spatial variability in term of characterization factors. The generic USEtox value is quite close of the global aggregated value of our modified version of USEtox : the addition of the link through groundwater, combined with the speciation accounting, seems to poorly influence the freshwater ecotoxicity of metal emitted to soil.

Groundwater movement is unpredictable and invariably changing. The assumption we made as saturated aquifer and in equilibrium with subsoil should be explored more. Also, the porosity might change based on groundwater position, soil characteristics, aquifer's type and structure since this is a highly specific scenario.

Soil to water fate and characterization factors can be studied based on their values with an archetype approach and their spread around the globe. In this way the highest and lowest emitters, potential risk of contaminating other compartment (based on wind flow, flux, rain etc.) could be identified and remediation or preventative measured can be taken to avoid future metal contaminations.

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CHAPTER 5 GENERAL DISCUSSION

This study made the first attempt in Life Cycle Impact Assessment to calculate metal toxicity from soil to water including speciation and the major interactions between soil, groundwater and freshwater compartments. With the inclusion of watersheds in our calculation, the user would be able to know the metal contribution from soil or watershed cells to the downstream water bodies. The results of the intersection between soil & watershed and water station locations will allow the user to directly measure the metal contamination from soil to freshwater in a very specific region. The soil to water fate and characterization factors, partition coefficients and water partition coefficients are all included with the results and it can be easily used and operationalized in the LCA community.

The method followed in this study can also be applied to other heavy metals for soil to water toxicity calculation for determining potential aquatic impacts from soil metal emission. Since WHAM 7 is applicable to 46 metals, this methodology in this study can be adapted. Using this method is recommended since it will greatly increase the credibility of the results for risk analysis and in decision and policy making.

Originally, the research hypothesis was: ignoring the deeper soil layer and groundwater and the connection between soil layers and surface water, we are introducing bias in our calculation. After the modifications within USETox, however, the generic USEtox calculated values are quite close of the global aggregated value from the modified version of USEtox. The aggregated fate and characterization factors are both within the acceptable uncertainty range of LCA with default USETox calculated values. The addition of the link through groundwater, combined with the speciation seems to poorly influence the freshwater ecotoxicity of metal emitted to soil. Nevertheless, the study is conducted only on Zn and the results might not reflect the same findings when other metals will be considered.

The spatial variability in FF_{sw} around the world ranged over two orders of magnitude with a median value of 4.23E+01 days. The generic USETox value for FF_{sw} is 4.78E+01 days, which is very close the global median calculated by default USETox. Although all the regions showed larger spatial variability in native resolution (watershed) K_d s, which were calculated from topsoil and subsoil K_d s within that area of that specific watershed (5 orders of magnitude for Australia, Canada, USA, 6 orders of magnitude for Mexico & C.America and Russia, 7 orders of magnitude

for Asia, Europe and S.America and 16 orders of magnitude for Africa), the soil-to-water metal fate factors (FF_{sw}) showed a variability of 2 orders of magnitude which is within USETox's acceptable uncertainty range for results (Sébastien Humbert, Schryver, Bengoa, Margni, & Jolliet, 2014). Interestingly, 80% of the total number of calculated native resolution FF_{sw} varied within the same order to magnitude ($1.71\text{E}+01$ to $8.2\text{E}+01$ days) which means a single value from this range can represent global soil to water fate factor.

The calculated native resolution scale soil to water characterization factors (CF_{sw}) varied over 3 orders of magnitude at the global scale with the most probable value for (sub) watershed CF_{sw} being $9.55\text{E}+04$ PAF.day.m³/kg. The USETox default CF_{sw} for soil to water is slightly higher than our calculated value ($1.36\text{E}+05$ PAF.day.m³/kg), but again, falls within the acceptable uncertainty range in LCA (Sébastien Humbert et al., 2014).

When a closer look is taken at the median values for the regionalized CF_{sw} for the continents/regions, the calculated generic USETox soil to water characterization factors are over-estimated for Africa ($2.43\text{E}+05$ PAF.day.m³/kg), Australia ($1.84\text{E}+04$ PAF.day.m³/kg), Canada ($5.75\text{E}+04$ PAF.day.m³/kg), Europe ($4.10\text{E}+04$ PAF.day.m³/kg), Mexico & C. Americas ($3.35\text{E}+04$ PAF.day.m³/kg), Russia ($1.16\text{E}+04$ PAF.day.m³/kg), South America ($4.48\text{E}+04$ PAF.day.m³/kg) and USA ($1.31\text{E}+04$ PAF.day.m³/kg) with the exception of Asia ($4.84\text{E}+05$ PAF.day.m³/kg) although within the acceptable uncertainty ranges (2 orders of magnitude) for all of them (Sébastien Humbert et al., 2014).

The regionalized freshwater K_{pss} and K_{DOC} at the watershed scale varied over 7 and 5 orders of magnitude across the globe. Given that, the K_{pss} and K_{DOC} found in Gandhi et al. (2010) and Dong et al. (2014) for Zn varied over 1-2 orders of magnitude over Europe. Given that, our values were calculated from all aquatic data around the globe, it is justified that there will be larger variation in the results than calculated only for Europe. Worldwide soil-water transfer coefficients for soluble Zn also varied over a wide range (15 & 16 orders of magnitude for top and subsoil). However, at least 80% of the values for top and subsoil were within 2 orders of magnitude with median K_d value, ($3.12\text{E}+04$ L/Kg and $1.66\text{E}+04$ L/Kg for topsoil & subsoil) so in case of unavailability of soil data, median K_d value can be used. The K_d s found in Plouffe et al. (2016) ranged over 5 orders of magnitude for true solution Zn which is also the calculated soil K_d range for this study when we consider only the most frequent values ignoring the outliers.

The regionalized bioavailability factors (BF) varied over 2 orders of magnitude across the globe with a median value of $3.85\text{E-}01$ and an average value of $4.07\text{E-}01$. Compared with the values found in Gandhi et al. (2010) ($1.32\text{E-}1$ to $9.79\text{E-}2$) and Dong, Gandhi et al. (2014) ($1.9\text{E-}1$ to $7.4\text{E-}1$), less variations are expected since their studies were limited for Europe. Our median and average values of BF are in the same order of magnitude for the entire world, however, it is not because there are little variations in worlds' water properties rather lack of aquatic data available.

The regionalized EF varied over 3 orders of magnitude across the globe with a median value of $4.69\text{E+}03 \text{ PAF.m}^3/\text{kg}$ and an average value of $5.79\text{E+}03 \text{ PAF.m}^3/\text{kg}$. Our calculated value is very close with the USETox generic EF value ($2.84\text{E+}03 \text{ PAF.m}^3/\text{kg}$). For Europe, effect factor varied over 1 order of magnitude (median = $2.41\text{E+}03 \text{ PAF.m}^3/\text{kg}$) as also found by Gandhi et al. (2010). For Dong et al. (2014), their EF for Europe stayed within the same order of magnitude and with the results of USETox calculated EF.

The consideration with groundwater being all saturated aquifer and in equilibrium with subsoil compartment should be explored more. Also, the porosity might change based on groundwater position, soil characteristics, aquifer's type and structure since it depends on specific scenario. An archetypical approach might be followed to categorize the impacts as in soil to water fate and characterization factors from available soil and water quality data. Different types of soils can also be identified and grouped together to have range of values of fate and characterization factors and other influential parameters.

CHAPTER 6 CONCLUSION AND RECOMMENDATIONS

6.1 Summary of the findings

The calculated values of soil to water fate and characterization factors show that the effects of modifications within the USEtox and the consideration of metal speciation are more pronounced in the water compartment than in soil. In higher resolution, the difference in both fate and characterization results are differentiable, however, all these modifications and considerations seemed to slightly influence the overall results.

The connection between soil and water within USEtox is one of the important features of this study. This is a first step in modifying USEtox and it allows us to get the results with all the compartments are connected together. Globally, we assumed that 25% of the total precipitation is leaching from the soil. Based on the soil type, pH, temperature, infiltration capacity, climate etc. it can be a very regionalized event which should be investigated more.

Gandhi et al. (2010) had calculated fate and characterization factors with the European aquatic data. The study created several water archetypes with similar physiochemical properties (pH, Hardness and DOC). It was recommended in Clearwater consensus in Diamond et al. (2010) to work further with the water archetypes for the worldwide aquatic data. Plouffe et al. (2015) and Plouffe et al. (2016) had also used the archetype approach and made 518 soil archetypes all over the world considering important soil characteristics (pH, CEC, Texture, Organic matter and carbonate content) (Diamond et al., 2010; Gandhi et al., 2010; Plouffe et al., 2015, 2016). The aim of the archetype creation however was not only to aggregate data or managing unavailable ones but also to impose background metal concentrations on individual group of archetypes. However, the archetypical approach is not considered in this study, rather, fate and characterization factors from soil to water are calculated for individual HWSD (HWSD-database, 2014) soil and watershed (A.-M. Boulay et al., 2018; WUCLA, 2017) cells. Later, worldwide available water properties are collected, we performed speciation, and fate and characterization from soil (watershed) to water are calculated. This is a very first project that connects topsoil, subsoil & groundwater together and while also including regional parameters with locations.

To calculate the fate and characterization factors for watersheds, it was explicitly assumed that the K_d of a single soil unit is equally divided within its sharing sub-watersheds. The minimum, maximum and average values were calculated from the K_d values that we have calculated during

the speciation calculation. Since watershed is directly linked with a specific water body, if the partition coefficients are known, the fate and characterization factors can be calculated.

Some of the limitations of this study which can be further investigated for research purposes are discussed in the next section.

6.2 Limitations and Recommendations

This work was focused on bridging the gap between soil, subsoil & groundwater and freshwater environment along with speciation. While the natural physiochemical interactions between metal, soil and water are complex, incorporating all equations related to inter-media interactions in one place will not only require an enormous amount of data (which is challenging for any field of science) but also will increase parametric uncertainty to the potential impacts calculated in LCA and defying the assumption of ‘parsimony’ within USETox. Here is a list of findings that are considered as the limitations of this research and also will serve as recommendations for future improvements.

1. We have considered subsoil compartment as a proxy for groundwater. In reality, groundwater network a vast subsurface network and everchanging. Although hydrogeological mapping could be obtained for specific regions, but then we also should be considering the hydrogeologic activities that take place in the subsurface environment. Given that there is no life within the subsurface (or at least, human health and ecosystem are not directly impacted by it) environment, we will be needing data to perform the bioavailability and effect calculations which at the moment is not available. This aspect might be explored in future.

2. Only soluble Zn fractions are considered to be mixing up with the groundwater and thereby with the freshwater. This assumption might be biased inclining toward over-estimated Zn fractions is allocated in the surface water system. Also, we have ignored the lateral movement in the subsurface environment and only considered the vertical flow. In reality water flows laterally from higher elevation point to the lower one.

3. Inside USETox, it is considered that. Only 25% of the water leached from soil from precipitation. This assumption may be valid considering the global aspect of LCA but for specific regions (regions with very high slope or flat land), it might not hold true.

4. We have aggregated fate and characterization data from a smaller to bigger regions (smaller watershed to bigger watersheds and from a region to country or continent) to get soil to water fate and characterization factors assuming the same aquatic properties are maintained over that aggregated geographic area. It might be okay for a low resolution but when one needs to focus on a specific part of the land/watershed or water, more information on the water properties of that specific location is required. More research is needed to find out to what extent the proxies are acceptable when data are not available.

5. According to Plouffe et al. (2015), WHAM 6 (WHAM7 is used in this study which is an updated version of WHAM6) had not been tested and validated for calcareous soils. It does not imply that this model cannot be used for speciation calculations on calcareous soils, however, there are few soil types for such soils and the data should be used with caution. Perhaps, validating WHAM7 for calcareous soils would be a good idea in future (Lofts, 2012).

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APPENDIX A – ELECTRONIC SUPPLEMENTARY MATERIAL-1(ESM 1)

Modeling of the groundwater compartment within USETox:

Surface area of subsoil & Groundwater compartment is considered same as the topsoil area. Margat (2008) has listed the active exchange volumes for aquifer for global and continental subterranean environment. For this modeling, we consider all the aquifer is saturated and in equilibrium with subsoil. For use in default USETox setting, the average surface area is calculated from the listed values in Margat (2008). The depth of the subsoil & groundwater compartment is kept as 1m , which also corresponds to database's indicated depth (HWSD-database, 2014). Here is a list of landscape properties for the subsoil & Groundwater compartments used inside USETox.

Table A5 Properties of the Subsoil & groundwater compartment

	Unit	Continental	Global
Area	m ²	4.37E+12	6.40 E+12
Depth	m	1	
Volume	m ³	4.37E+12	6.40E+13
Fraction of soil in Subsoil & Groundwater		0.52	$porosity = (1 - \frac{soil\ bulk\ density}{soil\ particle\ density}) * 100$ <p>Average soil bulk density for HWSD soil samples is 1.39 g/cm³ (HWSD-database, 2014)</p> <p>Soil particle density = 2.65 g/cm³</p>
Fraction of water in Subsoil & Groundwater		0.48	

Listed value for different continents are from Margat (2008):

Table A6 Continental SubSoil & groundwater volume from Margat (2008)

	<i>Unit</i>	<i>Continental</i>	<i>Global</i>
<i>Europe</i>	m ³	1.4 E+15	10.7 E+15
<i>Asia</i>	m ³	3.4 E+15	10.7 E +15
<i>Africa</i>	m ³	2.5 E+15	10.7 E +15
<i>North America</i>	m ³	1.9 E+15	10.7 E+15
<i>South America</i>	m ³	1.2 E+15	10.7 E+15
<i>Asutralia</i>	m ³	0.3 E+15	10.7 E+15

For the soil to groundwater fate and characterization factors (FF_{sw} & CF_{sw}), if calculating from the native soil resolution as in HWSD soil units, the individual values of soil bulk density can be used to calculate porosity for each subsoil & groundwater units (same HWSD MU_Globals). For any soil in the world however, the measurement of bulk density and porosity is challenging and we recommend using the default value listed here which is 48% porosity with 1.39 g/cm³ reference bulk density. The listed bulk densities for subsoil in the database range from 1.09 to 1.96 g/cm³. Similar types of soil units are observed within watersheds and using a generic value for bulk density and porosity will not create a bias rather limit producing erroneous results.

Consideration prioritization of different geographical regions and Choice & treatment of aquatic data:

For Europe, data for calculation is taken from FOREGS database. This data has been used to make freshwater archetypes in Gandhi et al. (2010) and Dong et al. (2014). There are few places in Belgium and Switzerland where both GEMStat and FOREGS stations were present, only latter one is considered to maintain the central tendency of the data as recommended in Diamond et al. (2010).

In terms of completeness of the data, only the stations in GEMStatPortal (2017) which listed at least pH, DOC, alkalinity/hardness/CaCO₃, Na⁺, Mg²⁺, Al³⁺, Ca²⁺, K⁺, SO₄²⁻ and Cl⁻ values were considered.

Wiken (1996) has classified Canada into 15 Ecozones and 5 marine ecozones based on the regions' climate, landforms/surface materials/soil types, water quality, wildlife, flora and fauna which stayed stable over a long period of time. Provided that human activity can change the climate and damage the soil/water. The boundaries are defined as, for example: arctic ecosystem characteristics are different than neighboring boreal ecosystem or the wetland ecosystems are different than the adjacent dry-upland ecosystems (Wiken, 1996). Detail description of each ecozones can be read from Wiken (1996). Gandhi, Huijbregts, et al. (2011) used freshwater properties from Canadian ecozones to compare the changes in CFs across ecoregions (Gandhi, Huijbregts, et al., 2011). Since GEMStatPortal (2017) stations for Canada were only located around the St-Lawrence river basin and 2 stations on the east coast, choosing the ecoregion specific data sounded a more exhaustive and unified approach. It is important to mention that all these Canadian stations were on the proximity to the US-Canada border.

For USA, none of the GEMStatPortal (2017) stations contributed to the data that we needed for the calculations. We supplemented the lack of data from GEMStatPortal (2017) for Canadian stations based on their proximity. For example, we have divided the map of USA into 3 sections (Figure A8). The first one being the Mississippi river watershed which consists of many sub-watersheds. Zn from all the sub-watersheds that fell under Mississippi are considered to be contributing to the Mississippi river. This watershed is adjacent to the St-Lawrence basin for which we had data from the GEMStatPortal (2017). These stations are well dispersed in the watershed and there are very little variations in their values of water properties from one to another. It is reasonable to assume their properties will not be drastically different and will not create a bias if we use them as proxies

to their adjacent water bodies. Similarly, the sub-watersheds that are situated left of the Mississippi (named as west coast) and we used a proxy for them from ecozone-13 (pacific maritime) aquatic data since it is (1) in proximity and (2) similar landscape features for most of the regions i.e: tall trees, most rainfall, long & deep fjords, mountains, variations in nature. The sub-watersheds on the right side of Mississippi are taken from the 2 water station from GEMStatPortal (2017) located on proximity to Maine and New Hampshire. Dissolved background Zn concentration for USA are obtained from ATSDR (2005) which is an average of all available Zn concentrations in US lakes.

For Mexico and Central America, all of the stations were located on Panama and since they both possess similar type of landscape/soil cover, surrounding water body we have chosen the average of the properties of all Panama stations corresponding to all sub-watersheds in this area.

In South America, Amazon (covers 33% of the land area) and Parana are the two biggest watersheds. Most of the water stations from GEMStatPortal (2017) fell within these two big watersheds. We averaged the water quality data over a bigger watershed (Amazon or Parana) and performed the calculation. For the rest of the sub-watersheds which did not fall under the abovementioned watersheds, calculations are done with all averaged water quality properties of the whole region.

Russian Federation possessed many water stations from GEMStatPortal (2017). Aggregation from sub-watershed to parent watershed are considered whenever any water stations are available to calculate fate and characterization factors for most watersheds possible, although results are presented in sub-watershed level. If no aquatic data were available, average of all Russian water properties are used for calculation. Since Russian water quality data are more thorough than others, it is not included while performing calculations for Asia or Europe.

Water stations were scatterly distributed around lower African regions. Fate and characterization factors are calculated for the watersheds that the stations are situated upon, average properties are used for the rest.

For Asia, the water properties from Japan were used since this is the only station in that continent and for Australia, world average value of all the water properties are used for calculations.

Background Zn Concentration: When available, we have used the listed dissolved Zn concentration from the database and literature for Zn speciation calculation (BGS_NERC, 2017; GEMStatPortal, 2017; Shiller & Boyle, 1985).

Table A7 Shows the source of data and the justification of using the data to perform the fate and characterization calculations.

Table A7 Region specific data choices for fate and characterization calculations.

Region	Sub-division	Origin of data	Method	Justification
Asia	None	GEMStatPortal (2017)	Proxy: Data from a station in Japan aggregated over entire region	Only available data for Asia and the station has nearly 8 years of data for different seasons.
Africa	None	GEMStatPortal (2017)	Exact locations where available on the watersheds; and African water average as proxy where no water data available	30 stations in lower part of Africa Only. Data taken over a period of 10 years at different seasons.
Australia	None	GEMStatPortal (2017) and (BGS_NERC, 2017)	Proxy: World water average	No other data available for this region or at the proximity.
Canada	Ecozone 1& 2	Gandhi, Huijbregts, et al. (2011) and Wiken (1996)	Aggregated data over a region for ecozones	The ecozones have similar landscape features, flora and fauna, it is reasonable to assume the water bodies possess similar features too.
	Ecozone 3			
	Ecozone 4			
	Ecozone 5			
	Ecozone 6			
	Ecozone 7			
	Ecozone 8			
	Ecozone 9			
	Ecozone 10			
	Ecozone 11			

	Ecozone 12			
	Ecozone 13			
	Ecozone 14			
	Ecozone 15			
Europe	Point locations on map	BGS_NERC (2017)	Exact location used	Completeness of data, Reliability: These data were used in several literature (Dong et al., 2014; Gandhi et al., 2010)
Mexico and Central America	None	GEMStatPortal (2017)	Aggregated data from stations located in Panama	Only available data for this region and exhibits similar landscape features. All the stations over Panama possessed very identical water properties.
Russian Federation		GEMStatPortal (2017)	Aggregation to larger watershed where available. For the rest, average Russian water properties data were used.	Many stations all over the region.
South America	Amazon basin	GEMStatPortal (2017)	Aggregation to Amazon & Parana watershed. Average water properties data of this region are used for the rest.	Big watersheds in South America, dominates the southern regions.
	Parana basin Rest of the watersheds			
USA	Mississippi river watershed	GEMStatPortal (2017) and Gandhi, Huijbregts, et al. (2011)		Proximity : Data were taken from stations located in Canada and close to USA water bodies.
	East Coast and			
	West Coast			

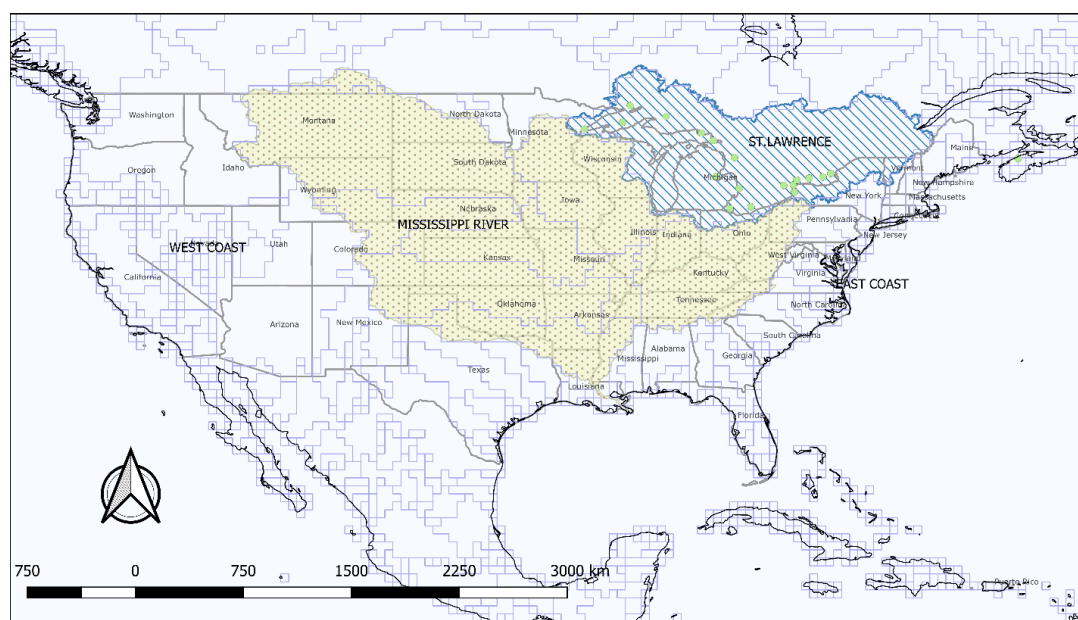


Figure A8 Map of USA subdivided into 3 sections and proximity of the Canadian stations from the GEMStatPortal (2017) database justifies the use of those data as proxies for toxicity calculations within the USA

Aggregated CFsw s over different regions:

Table A8 Aggregated soil to water fate and characterization factors for different regions

<i>Regions</i>	<i>FFsw(agg)</i> <i>(Days)</i>	<i>CFsw(agg)</i> <i>(Days.PAF.m³/kg)</i>
<i>Asia</i>	5.89E+01	2.48E+05
<i>Africa</i>	3.68E+01	4.89 E+04
<i>Australia</i>	2.42 E+01	1.80 E+04
	7.56 E+01	6.12E+04
<i>Europe</i>	4.03 E+01	5.13 E+04
<i>Mexico & Central America</i>	3.24 E+01	3.41E+04
<i>Russian Federation</i>	2.39E+01	1.11E+04
<i>South America</i>	2.32E+01	4.39E+04
<i>USA</i>	2.60E+01	5.24E+04

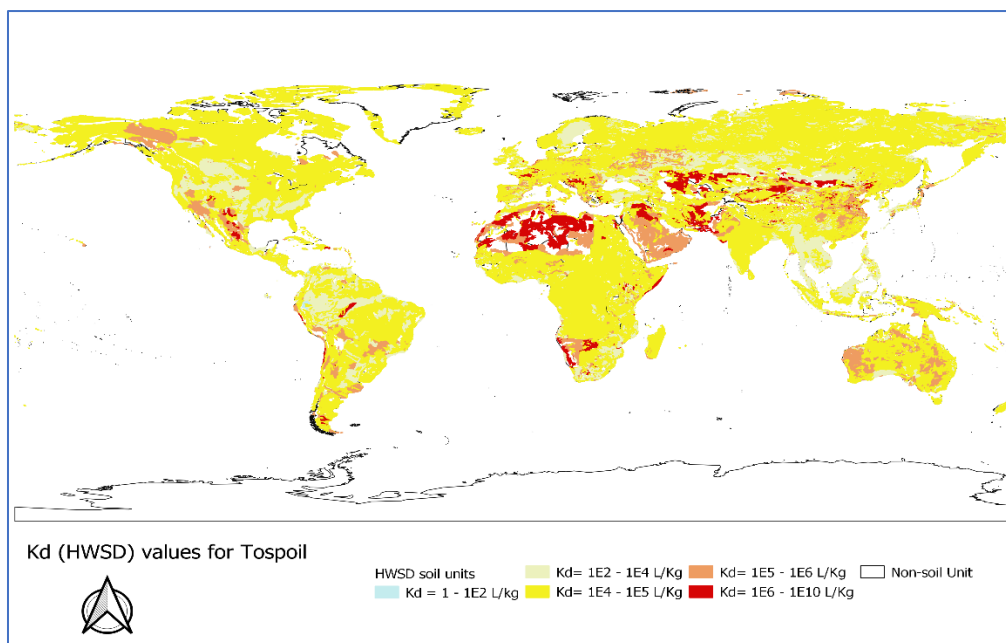


Figure A9 Topsoil partition coefficient K_d (L/Kg) for all HWSD topsoil Units

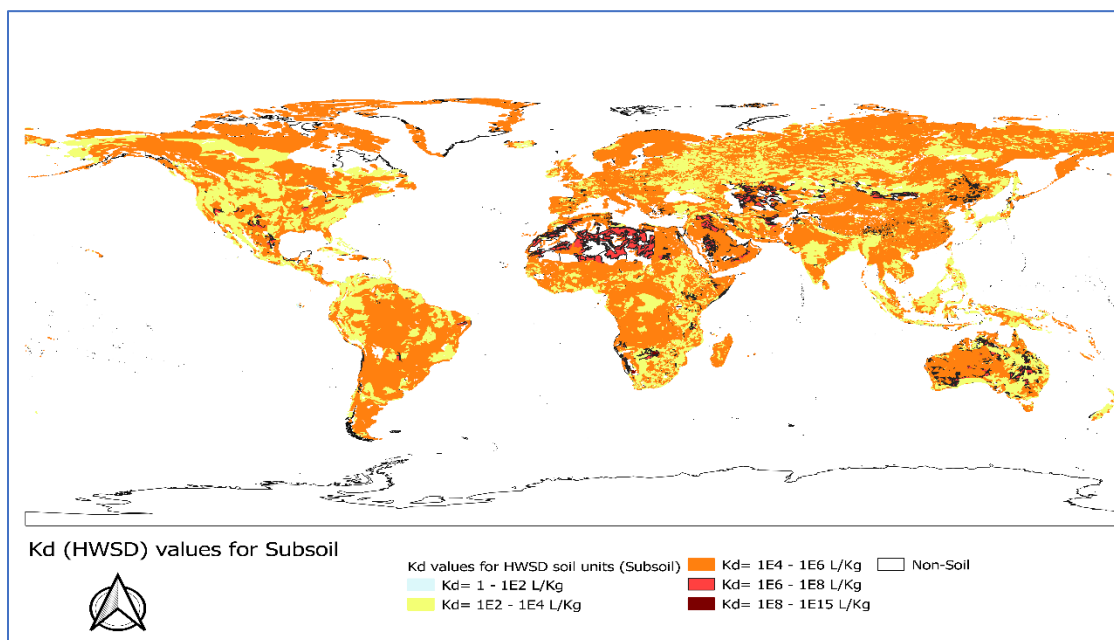


Figure A10 Subsoil partition coefficient K_d (L/Kg) for all HWSD subsoil Units

APPENDIX B – ELECTRONIC SUPPLEMENTARY MATERIAL-2(ESM 2)

APPENDIX-B-ESM_2-
RIFAT.xlsx

APPENDIX C – ELECTRONIC SUPPLEMENTARY MATERIAL-3(ESM 3)

APPENDIX-C-ESM_3-
RIFAT.xlsx